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THE
THEORY OF SOLUTIONS
OF
HIGH POLYMERS

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THEORY OF SOLUTIONS
OF
HIGH POLYMERS

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PREFACE

My interest in this subject, interrupted during the war, was first stimulated by experimental work which was being carried out on solutions of high polymers and, in particular, of the accurate measurements, which were being made at the laboratories of the British Rubber Producers' Research Association, of the thermodynamical properties of the rubber-benzene system.

The theory of solutions of high polymers involves a general examination of the statistical mechanics of mixtures, treated as co-operative assemblies. While making some contribution to the general study of co-operative assemblies, the particular application which has been kept in mind has been that to solutions of high polymers. It is from this point of view that this monograph has been written, although discussion of co-operative assemblies has been included in so far as it is germane to our subject or is necessary in order that the methods which have been employed here may be understood. The general aim has been to give an account of the mathematical advances in the treatment of solutions of high polymers which have been made during the last decade.

The introductory chapter is designed to describe the model of a liquid which is used and to recall the nature of a partition function and its use in the theory of solutions. The application of the particular model to solutions of high polymers and the difficulties which arise in the evaluation of their statistical and thermodynamical functions is then examined. The next two chapters develop the theory and examine its application to the available experimental data. Chapter V is devoted to an examination of the effect of the energy of mixing, and in the final chapter various causes to which the remaining discrepancy between experiment and theory may be due, and on which further research is required, are examined.

It is a pleasure to acknowledge my indebtedness to Dr. E. A. Moelwyn-Hughes and to Mr. A. B. Pippard, whose kindness in reading the manuscript has ensured greater clarity of presentation than would otherwise have been the case. I also wish to express my thanks to the officers of the Clarendon Press for their unfailing consideration and helpfulness, and my appreciation of the skill of their craftsmen. Nor can I close this preface without paying a tribute to the memory of those who first guided me in research at Cambridge, and whose deaths during the war were not only a personal loss but have left the scientific world very much poorer: John Keith Roberts and Ralph Howard Fowler.

A. R. M.

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March 1948

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I

INTRODUCTION

1.1. Liquid mixtures of which one of the components is a high polymer behave in a markedly different way from solutions of components of low molecular weight. A substance of relatively low molecular weight dissolves in a solvent to a precise maximum concentration. On the other hand, in the presence of suitable liquids, high polymers first swell, imbibing liquid without themselves being dispersed. If the polymer is insoluble, nothing further happens; in a solvent the high polymer gradually loses its form and ultimately disperses to form a solution. For substances of relatively low molecular weight in the region of dilute solutions, various properties such as the vapour pressure, the osmotic pressure, and the depression of the freezing-point depend in a very simple way on the concentration of the solution which is described as ideal. Solutions of high polymers show departures from all these simple laws. It is the purpose of this treatise to develop the statistical mechanics of solutions of high polymers and thus to describe the theory which accounts in large measure for these departures from ideal behaviour. First it will be advisable to consider briefly the theory of two classes of simpler liquid mixtures, usually designated as perfect and regular solutions, of which strict definitions will be given below. This procedure has the further advantage that it will present in terms of simple and familiar systems some of those basic principles of statistical mechanics which are to be used in this monograph.

1.2. The laws of extremely dilute solutions were first elucidated by van 't Hoff. The equations which he obtained give a correct phenomenological description of the relations between the vapour pressure, the osmotic pressure, and the depression of the freezing-point, &c., that is, given any one of these, the deduction of the others is given correctly by van 't Hoff's equations. His derivation of these equations cannot be regarded, however, as satisfactory, for his basic assumption is that the solute molecules in dilute solution can be treated as a perfect gas, and this is inconsistent with thermal data.[†] For pairs of substances whose behaviour is at least nearly ideal it is found that the heat of dissolution of a gas in a liquid is approximately equal to its heat of condensation; that of a liquid in a liquid is zero; that of a solid in a liquid is equal to its heat of fusion. Such results indicate that in solution the solute molecules must be regarded as having a status which is thermodynamically indistinguishable from the liquid state. No account which starts by assuming that the solute molecules behave as a gas can then provide an adequate theory. Furthermore, much confusion has arisen as a result of the unjustifiable extrapolation of van 't Hoff's laws to high concentrations. A correct thermodynamical formulation of the laws of ideal solutions was given by van Laer[‡] using the methods of Willard Gibbs. A notable step forward was taken when G. N. Lewis[§] gave a precise definition of a perfect or ideal liquid mixture and formulated the laws obeyed by them. An elementary derivation of these laws in terms of thermodynamical cycles was given by Washburn.[||]

It can be shown thermodynamically that necessary conditions for two substances to form an ideal mixture are that when they are mixed at constant temperature and pressure there is no change of volume or energy.[††] It is also necessary that the different kinds of molecules can be treated as spheres of approximately the same size; it has been shown that this condition can be stated more precisely by saying that the molecular volumes of the two species should not differ by a factor of more than two.[‡‡] The behaviour of ideal solutions is summed up most elegantly and simply in Raoult's law. It can be expressed by saying that at constant temperature and external pressure, the partial vapour pressure of any component of a liquid mixture bears a constant ratio to its molar fraction.† The most satisfactory way in which to derive these laws is to construct the partition function for the assembly and from it to determine the free energy. This procedure, which is of quite general application, will be illustrated in the succeeding paragraphs. First it is desirable to recall the nature of a partition function and to describe the liquid model which will be used.

[†] Compare Kendall, J., *Trans. Faraday Soc.* **33** (1937), 1.

[‡] van Laer, J. J., *Z. physikal. Chem.* **15** (1894), 457.

[§] Lewis, G. N., *J. Amer. Chem. Soc.* **30** (1908), 668.

[||] Washburn, E. W., *Z. physikal. Chem.* **74** (1910), 385.

[††] It should be noted that zero energy change on mixing does not require that the interaction energies be zero. (Cf. Guggenheim, E. A., *Proc. Roy. Soc.* A **148** (1935), 304, equation (6)).

[‡‡] Bernal, J. D., quoted by Fowler, R. H., and Guggenheim, E. A., *Statistical Thermodynamics* (Cambridge, 1939), p. 351 f.n.

Partition functions

1.3. The quantal description of the state of an assembly is given completely by the specification of its eigenfunction. In the quantal formulation of statistical mechanics, unit weight is allotted to each non-degenerate state of the assembly. When we speak of a degenerate state of weight ϖ we refer simply to a set of states, ϖ in number, between which no distinction is made in terms of our particular description of the state. If the eigenfunction of the assembly is expressed in terms of the eigenfunctions of its constituent systems, three alternative, and familiar, sorts of statistical formulae are obtained according to the symmetry restrictions which are imposed on the eigenfunctions of the assembly. On the other hand, if, as is often the case, one is concerned only with the macroscopic properties of the whole assembly, these alternatives need not be considered separately. In describing the equilibrium properties of an assembly in thermodynamical terms one is content with a less precise description than can be obtained formally from quantum mechanics, so that the state of the whole assembly is specified by a description of a small number of macroscopic properties. In general, at least three such quantities‡ are required and they are to be chosen from the internal energy (E), temperature (T), pressure (p), volume (V), partial potential (μ), and number (N) of particles in the assembly according to which of these quantities it is convenient to choose as independent variables.†

---

† Henry's law is a special case of this.

‡ Or two quantities if the masses of the components, and therefore the parameters N, are fixed.

1.4. In the most common specification of an assembly the temperature, volume, and the numbers of molecules of the components are taken as the independent variables. If ϖ_r is the degeneracy of the quantum state of energy ϵ_r, then the sum of terms $\exp(-\epsilon_r/kT)$, each weighted according to the degeneracy of the corresponding eigenstate, and summed over all the states of the assembly, is the (ordinary) partition function for the systems of which the assembly is composed. Thus

$$f = \sum_r \varpi_r \exp(-\epsilon_r/kT). \tag{1.1}$$

The partition function, which is a dimensionless quantity, summarizes in a convenient mathematical form the way in which the energy of the assembly is partitioned among the individual systems of which it is composed. It is the analogue of Gibbs's canonical ensemble. The related thermodynamical potential is the Helmholtz free energy which is given by

$$-\frac{A}{kT} = \log \sum_r \varpi_r \exp\left(-\frac{\epsilon_r}{kT}\right). \tag{1.2}$$

The corresponding expression in terms of the macrodescription of the assembly gives a well-known formula

$$f = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} V$$

for the partition function per molecule. We must now consider the partition function for the whole assembly.

1.5. The energy of an assembly is the sum of (*a*) the kinetic energy of translation of the individual molecules or atoms (systems) of which it is composed, (*b*) the rotational, vibrational, and electronic energies of the individual systems, and (*c*) the configurational energy of the assembly as a whole, due to the interactions between its component systems. Corresponding to this† the partition function $F(T)$ of the assembly splits into three factors. Thus

---

† There may sometimes be additional parameters required; e.g., the fractions of a given quantity of hydrogen which are in the para and ortho states, or the fractions of a given quantity of a component which are liquid and vapour.

$$F(T) = \{l(T)j(T)\}^{N}\Omega(T), \tag{1.3}$$

where the partition function corresponding to the translational motion of a single particle is given by the product of $l(T)$ and the configurational (volume) factor per system, which is here included in $\Omega(T)$, $j(T)$ is the partition function of a single particle corresponding to the energy which arises from all its internal degrees of freedom, and $\Omega(T)$ is the configurational term for the whole assembly. If the rotational and vibrational motions may be treated as independent, then $j(T)$ splits into factors: $r(T)$ for the rotational energy, $v(T)$ for the vibrational energy, and $e(T)$ for the electronic energy.

1.6. In the applications which are to be discussed in the following chapters, we are to consider the equilibrium of matter in bulk. Consequently, we shall be concerned to distinguish only between different macrostates of the assembly, lumping together all microstates for which the whole assembly has the same configurational energy. In effect, this assumes that $l(T)$ and $j(T)$ are independent of the configuration of the assembly as a whole. In other words, there are $g(W)$ states of the assembly with configurational energy W between which we do not distinguish in terms of the particular description of the assembly which is relevant to our purpose. Thus the determination of the partition function reduces to the evaluation of the configurational factor $\Omega(T)$. In somewhat less general terms it can be expressed thus: consider an assembly, specified by the parameters N which are related‡ to the numbers of molecules of the different species. Let the assembly be in one of $g(N)$ configurations in each of which the potential energy is $W(N)$. The configurational term is then given by the multiple integral

$$\Omega(T) = \int \ldots \int \exp\{-W(N)\}/\boldsymbol{k}T \prod (d\omega)^{N}, \tag{1.4}$$

where $\prod (d\omega)^{N}$ is an abbreviation for the product of elements of volume for each type of molecule, equal in number to the number of molecules of that type, and is used to indicate that the integration is to be extended over all the space and velocity coordinates of all the systems. From what has been said already (§ 1.4), it is clear that, in terms of a description of the assembly relevant to our purpose, the partition function must consist formally of the sum of terms of the type

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† See § 1.10, equation (1.9).

‡ In addition to the numbers of particles of different kinds, there will also be parameters which give the numbers of pairs of neighbours of different kinds.

$$g(N)\exp\{-W(N)/kT\} \tag{1.5}$$

apart from factors arising from the effective free volume and the partition functions for the translational and internal degrees of freedom of each molecule. The essence of the problem is to determine the appropriate combinatory factor $g(N)$. To write an expression like (1.5) merely shifts the point of difficulty from the evaluation of the multiple integral in (1.4) to that of the appropriate combinatory factor $g(N)$.

1.7. A generalization of the idea of a partition function was given by Fowler,[†] who considered the statistical analogue of Gibbs's grand canonical ensemble. It provides a very powerful method and is usually called the grand partition function. In using the grand partition function the temperature, volume, and partial potential are taken as the independent variables, and the appropriate weight factor in the summation over all the states of the assembly is $\exp\{-(\epsilon_r-N\mu)/kT\}$. The grand partition function is defined by

$$Z = \sum_N \sum_r \varpi_r \exp(-\epsilon_r/kT)\lambda^N, \tag{1.6}$$

in which the sum is taken over all states of the assembly and over all values of the numbers of systems of each kind composing it. In this expression λ is the absolute activity which is defined by

$$\left(\frac{\partial G}{\partial N}\right)_p = \mu = kT\log\lambda, \tag{1.7}$$

where G is the Gibbs function. The 'thermodynamical potential' related to the grand partition function is given by

$$\frac{pV}{T} = k\log Z = k\log\sum_N\sum_r \exp(-\epsilon_r/kT)\lambda^N.$$

[†] Fowler, R. H., *Proc. Cambridge Phil. Soc.* 34 (1938), 382.

The corresponding expression for the grand partition function in terms of a macrodescription of the assembly is

$$Z = \sum_N \sum_W g(W)\exp(-W/\boldsymbol{k}T)(\lambda\phi)^N, \tag{1.8}$$

where ϕ includes the volume factor and the partition function per system corresponding tò the translational and internal degrees of freedom.

This brief description† of the nature of a partition function has been included because we shall have constant recourse to those methods of statistical mechanics, due to Fowler and Darwin, which use partition functions.

1.8. The simplest assemblies of statistical mechanics are those in which the interactions between the elementary particles of which the assembly is composed are so weak that they can be neglected. In this case the assembly can be regarded as a large number of virtually independent systems, and it is called an ideal or perfect assembly. If the interactions, while no longer negligible, are still small, one has a slightly non-ideal assembly. However, there are other assemblies in which the interactions are so important that the states of any distinct system are influenced in a fundamental way by which states of the other systems are occupied. Such assemblies are termed co-operative. The constituent systems of a co-operative assembly cannot be treated as independent, that is, the free energy (for example) is not simply the sum of the free energies of the constituent systems. The advances which have been made during the last decade in the application of statistical mechanics to liquids have followed from the recognition that a liquid forms a co-operative assembly.

Liquid models

1.9. Earlier discussions of liquids involved an unwarranted extrapolation of results which had been derived only for slightly imperfect gases. Such extrapolation was based on the assumption that a liquid does not differ in any essential way from a gas, being merely more highly compressed. It is correct that there is no discontinuity between gas and liquid, but such a formal identity overlooks the fact that an essential part of the treatment† of slightly imperfect gases is that the effective volume is not very much smaller than the total volume. Even at the critical point the effective volume is only about half the actual volume and in liquids it becomes even smaller. That is, the usual treatment of imperfect gases requires the assumption that the difference between the total and effective volumes is very much smaller than the total volume, while in a liquid the reverse is true, namely, the effective volume is very much smaller than the total volume.

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† For a more detailed description see Fowler, R. H., *Statistical Mechanics* (Cambridge, 1936), ch. ii; Fowler, R. H., *Proc. Cambridge Phil. Soc.* **34** (1938), 382; Guggenheim, E. A., *J. Chem. Phys.* **7** (1939), 103.

The simplest useful model of a liquid of symmetrical molecules is a collection of spheres packed together, not tightly (which would represent a crystalline solid), but not very far from tightly. It is clear that such a model has less order than a crystalline solid, but it retains a degree of order far different from the almost complete randomness of configuration which is characteristic of a gas. This model will be referred to as quasi-crystalline. Such a model ensures that the component molecules are allowed considerable freedom of movement; at the same time it secures a high degree of local order. That there is a high degree of local order in certain liquids at ordinary temperatures has been confirmed by X-ray analysis;‡ and it appears that, except in the neighbourhood of the critical point, a liquid is much more like a crystal than a gas.§ At temperatures well below the critical temperature the number of neighbours surrounding each molecule has a well-defined average value. The fluctuations about this average value are not serious; except for a rather unimportant fraction of centres in the liquid, they will not disturb the regularity of the geometrical relationship between each molecule and its closest neighbours, which, on the average, is very similar to that in a crystal. The fluctuations are, however, usually sufficient to destroy the long-range order, so that there is no regular geometrical relationship between a molecule and its more distant neighbours. On this model, which is the simplest that is in agreement with the available X-ray data on liquids, the essential difference between a liquid and a crystal is that whereas the former possesses a high degree of local order, which can be defined by an average coordination number, the latter, in addition, exhibits long-range order in the geometrical relationships between its constituent molecules.

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† With the exception of the treatment of condensed systems due to Mayer (Mayer, J. E., *J. Chem. Phys.* **5** (1937), 67; Mayer, J. E., and Ackerman, P. G., ibid. p. 74; Mayer, J. E., and Harrison, T. F., ibid. **6** (1938), 87, 101).

‡ Friedrich, W., *Phys. Zeit.* **14** (1913), 397; Debye, P., and Scherrer, P., *Gött. Nach.* **16** (1916); Debye, P., and Menke, H., *Phys. Zeit.* **31** (1930), 797; *Ergeb. d. Tech. Rontgenk.* **11** (1931); Bragg, W. L., *The Crystalline State, A General Survey* (G. Bell and Sons, 1933), p. 195; Gingrich, N. S., *Rev. Mod. Phys.* **15** (1943), 90; Finbak, C., *Skr. norske Vidensk. Akad.* **10** (1945).

§ This viewpoint has recently been elaborated and emphasized by Frenkel, J., *Kinetic Theory of Liquids* (Oxford, 1946). See also Meyer, K. H., *Zeits. f. physik. Chemie*, B **44** (1939), 383; *Helv. Chim. Acta*, **23** (1940), 1063; Meyer, K. H., and Boissonas, C. G., ibid. **23** (1940), 430.

1.10. It is a standard and well-known result of statistical mechanics† that the partition function of an assembly of N molecules of mass m which are confined to a volume V is

$$\left\{\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} j(T)\right\}^N \Omega(T) = \{l(T)j(T)\}^N \Omega(T), \qquad (1.9)$$

where the configurational term $\Omega(T)$ is given by

$$\Omega(T) = \frac{1}{N!}\int \ldots \int e^{-W(N)/kT}(d\omega)^N. \qquad (1.10)$$

Here $j(T)$ is the partition function for all the internal degrees of freedom (rotational, vibrational, electronic, and nuclear spin); $l(T)$ is the partition function for the translational motion of a molecule; $W(N)$ is the configurational potential energy of the assembly referred to that of the molecules at infinite separation as zero; the factorial is introduced to remove multiple counting of indistinguishable configurations; and $(d\omega)^N$ denotes the product of the N elements of volume to which the centres of the N molecules belong. The multiple integration is extended over the whole of the $3N$ dimensional phase space accessible to the molecules. For an assembly of non-interacting spherical molecules or for a liquid, neglecting molecular interactions, it can be shown that†

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† Fowler, R. H., *Statistical Mechanics* (Cambridge, 1936), § 2.6.

$$\Omega(T) = (ev)^N, \tag{1.11}$$

where v is equal to the effective free volume per molecule and is a function of V/N. This, however, can be of little practical interest on account of the neglect of the intermolecular forces.

1.11. For a liquid, the volume V in which it is contained is determined by the intermolecular forces. A useful approximation to take account of the interactions in a normal liquid is provided by the smoothed potential model, in which the configurational energy is replaced by its value averaged over all accessible configurations. This average value of the configurational energy can be written as

$$W = -N\chi,$$

where $-\chi$ is the average value of the molecular energy for all relative configurations of the given molecule and its neighbours; since the attractions are assumed to be short-range forces, only near neighbours will contribute appreciably to it, so that its value will be determined by the average number of near neighbours within a specified distance. It therefore follows that χ is a function only of the average volume per molecule. This model leads to the familiar result

$$\Omega(T) = (ev)^N \exp(N\chi/kT) = [v\exp\{(\chi+kT)/kT\}]^N. \tag{1.12}$$

In general, the configurational term $\Omega(T)$ given by the integral in equation (1.10) will reduce to the product of three factors. Thus it will be the product of a combinatory factor which arises from the number of distinguishable configurations of the systems of the assembly, a volume factor, such as $(ev)^N$, and a term which depends on the configurational energy, such as $\exp(N\chi/kT)$.

Derivations of the configurational term which are based on more precise physical models can be formulated. A model, due essentially to Mie,‡ in which the change in interaction energy as the molecule moves about its equilibrium position is allowed for by assuming that each molecule moves in a field corresponding to an isotropic three-dimensional harmonic oscillator, provides a useful comparison with a solid. A more refined model† in which the molecular energy is calculated directly from the interaction energy between pairs of molecules has also been examined. The factor e in equations (1.11) and (1.12) represents an essential point of difference between a liquid and a solid. It gives rise to an additional term k in the molecular entropy and specifies the greater disorder of the liquid.‡

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† Fowler, R. H., *Statistical Mechanics*, 2nd edition (Cambridge, 1936), § 13.1.

‡ Mie, G., *Ann. d. Physik*, **11** (1903), 657.

Partition function of a strictly regular solution

1.12. A mixture of molecules of two species i and j is said to form a strictly regular solution§ if (i) both types of molecule pack in the same way so that they have a common coordination number; (ii) the molecular volumes are sufficiently alike for a mixture of the two kinds of molecules to pack in the same way as each of the pure liquids; (iii) the ratio of the free volumes of the two pure liquids lies between 1 and 1·30; (iv) both the molecular volumes and the free volumes are unaltered when the two liquids are mixed at a given temperature and pressure, and (v) only closest neighbour pairs make any significant contribution to the potential (configurational) energy of the mixture.

An energy of mixing w_{ij} is defined so that if, in the two pure liquids, an interior molecule of type i is interchanged with an interior molecule of type j the total increase in the potential energy is $2w_{ij}$. If the average potential energy of a molecule of type i in the pure liquid is $-\chi_i$ and that of a molecule of type j in its pure liquid is $-\chi_j$, then the average energies of interaction of a pair of closest neighbour molecules i is $-2\chi_i/z$ and of a pair of closest neighbour molecules j is $-2\chi_j/z$, where z is the common coordination number of each pure species and of the mixture. If the average interaction energy of a molecule i and a molecule

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† Lennard-Jones, J. E., and Devonshire, A. F., *Proc. Roy. Soc.* A **163** (1937), 53; ibid. **165** (1938), 1.

‡ The discontinuity between the thermodynamical functions of liquids and crystals was first emphasized by Eyring (Hirschfelder, J., Stevenson, D., and Eyring, H., *J. Chem. Phys.* **5** (1937), 897) and by Lennard-Jones (Lennard-Jones, J. E., and Devonshire, A. F., *Proc. Roy. Soc.* A **163** (1937), 61).

§ Fowler, R. H., and Guggenheim, E. A., *Statistical Thermodynamics* (Cambridge, 1939), ch. viii.

j which occupy a pair of closest neighbour sites (that is, which are in contact) is V_{ij}, then

$$2w_{ij} = z(2V_{ij}-V_{ii}-V_{jj}), \tag{1.13}$$

where V_{ii}, V_{jj} have been written for $-2\chi_i/z$ and $-2\chi_j/z$ respectively.

1.13. Consider a particular configuration of the mixture of N_i molecules of type i and N_j molecules of type j in which there are zX closest neighbour $i-j$ contacts. The numbers of $i-i$ and $j-j$ closest neighbour contacts are then $\frac{1}{2}z(N_i-X)$ and $\frac{1}{2}z(N_j-X)$ respectively. The potential energy is therefore given by

$$W = -N_i\chi_i-N_j\chi_j+Xw_{ij}. \tag{1.14}$$

The configurational factor in the partition function of the mixture is, from equation (1.10), given by

$$\Omega(T) = e^{(N_i\chi_i+N_j\chi_j)/kT}\frac{1}{N_i!\,N_j!}\int\cdots\int e^{-Xw_{ij}/kT}(d\omega_i)^{N_i}(d\omega_j)^{N_j}. \tag{1.15}$$

First consider the special case of a perfect solution defined by w_{ij} zero; then

$$\begin{aligned}\Omega(T) &= e^{(N_i\chi_i+N_j\chi_j)/kT}\frac{1}{N_i!\,N_j!}\int\cdots\int (d\omega_i)^{N_i}(d\omega_j)^{N_j}\\ &= e^{(N_i\chi_i+N_j\chi_j)/kT}\frac{1}{N_i!\,N_j!}(N_iv_i+N_jv_j)^{N_i+N_j}. \qquad (1.16)\end{aligned}$$

With an error of not more than about 1 per cent. the arithmetic mean of the free volumes may be replaced by the geometric mean. Thus

$$\frac{N_iv_i+N_jv_j}{N_i+N_j} = \{v_i^{N_i}v_j^{N_j}\}^{1/(N_i+N_j)};$$

and with this approximation equation (1.16) reduces to

$$\Omega(T) = \frac{(N_i+N_j)!}{N_i!\,N_j!}\{ev_i\exp(\chi_i/kT)\}^{N_i}\{ev_j\exp(\chi_j/kT)\}^{N_j}, \tag{1.17}$$

giving the configurational factor in the partition function for a perfect solution. It should be noted that the first factor in equation (1.17) is the number of ways of arranging N_i indistinguishable systems of one kind and N_j indistinguishable systems of a second kind on an array of N_i+N_j sites. For the grand partition function of a perfect solution this gives

$$Z = \sum_{N_i,N} g(N_i, N_j)\exp\{(N_i\chi_i+N_j\chi_j)/\boldsymbol{k}T\}\{ev_i\, l_i(T)j_i(T)\}^{N_i}\times \\ \times\{ev_j\, l_j(T)j_j(T)\}^{N_j}\lambda_i^{N_i}\lambda_j^{N_j}, \quad (1.18)$$

where $g(N_i, N_j)$ is the combinatory factor, that is, the number of distinct configurations of the systems of which the assembly is composed with an energy W equal to $N_i\chi_i+N_j\chi_j$; in this example of a perfect solution $g(N_i, N_j)$ is equal simply to

$$(N_i+N_j)!/N_i!\,N_j!.$$

The partition function for a pure liquid is, from equations (1.9) and (1.12),

$$\{l(T)j(T)\exp(\chi/\boldsymbol{k}T)ev\}^N = \{L(T)\}^N. \quad (1.19)$$

Then the partition function for a given configuration of N_i molecules i and N_j molecules j which form a perfect mixture can always be expressed by $\{L_i(T)\}^{N_i}\{L_j(T)\}^{N_j}$ provided $L_i(T)$ and $L_j(T)$ are independent of the ratio N_i/N_j. The partition function for the system of N_i molecules i and N_j molecules j including all configurations is therefore

$$F = \frac{(N_i+N_j)!}{N_i!\,N_j!}\{L_i(T)\}^{N_i}\{L_i(T)\}^{N_j}, \quad (1.20)$$

in agreement with the form obtained (equation (1.17)) by evaluating the integral in equation (1.16). The grand partition function for a perfect solution is then given by

$$Z = \sum_{N_i,N_j}\frac{(N_i+N_j)!}{N_i!\,N_j!}\{L_i(T)\lambda_i\}^{N_i}\{L_j(T)\lambda_j\}^{N_j}. \quad (1.21)$$

1.14. The laws of perfect solutions can be derived immediately from the partition function. From equations (1.3) and (1.17) the free energy of the mixture is given by

$$\frac{A^l}{\boldsymbol{k}T} = -(N_i+N_j)\log(N_i+N_j)+N_i\log N_i+N_j\log N_j- \\ -N_i\{\log l_i(T)+\log j_i(T)+\log v_i\}-N_i-N_i\chi_i/\boldsymbol{k}T-$$

From equations (1.9) and (1.12) the free energy of the pure liquid i is given by

$$\frac{A_i^l}{\boldsymbol{k}T} = -N_i\{\log l_i(T)+\log j_i(T)+\log v_i\}-N_i-N_i\,\chi_i/\boldsymbol{k}T,$$

so that the free energy of mixing is given by

$$\frac{\Delta A^l}{\boldsymbol{k}T} = -(N_i+N_j)\log(N_i+N_j)+N_i\log N_i+N_j\log N_j. \tag{1.23}$$

Denote by μ_i^l the partial potential of the species i in the liquid mixture, and by $\mu_{i,0}^l$ the partial potential of the pure species i. If the Gibbs free energy of mixing is denoted by ΔG, then for a binary mixture it is defined by

$$G = G_i+G_j+\Delta G,$$

where G_i and G_j are the Gibbs free energies of the pure species and G is that of the mixture. At constant pressure and temperature

$$\left(\frac{\partial G}{\partial N_i}\right)_{T,p} = \left(\frac{\partial G_i}{\partial N_i}\right)_{T,p}+\left(\frac{\partial \Delta G}{\partial N_i}\right)_{T,p} \quad \text{(all } i\text{)}.$$

Thus

$$\mu_i^l = \mu_{i,0}^l+\left(\frac{\partial \Delta G}{\partial N_i}\right)_{T,p} \quad \text{(all } i\text{)}.$$

Thus, provided the pressure is small,

$$\mu_i^l = \mu_{i,0}^l+\boldsymbol{k}T\log\frac{N_i}{N_i+N_j}, \tag{1.24}$$

$$\mu_j^l = \mu_{j,0}^l+\boldsymbol{k}T\log\frac{N_j}{N_i+N_j}. \tag{1.25}$$

The free energy of the gas phase is given by

$$\frac{A^v}{\boldsymbol{k}T} = -N_i'\left\{\log\frac{l_i'(T)j_i'(T)V'}{N_i'}+1\right\}-N_j'\left\{\log\frac{l_j'(T)j_j'(T)V'}{N_j'}+1\right\}, \tag{1.26}$$

where primes are used to specify parameters of the gas phase. If the vapour of each species can be treated as a perfect gas, then the partial pressures in the gas phase are given by

$$p_i = N_i'\boldsymbol{k}T/V' \quad \text{(all } i\text{)}. \tag{1.27}$$

From equations (1.26) and (1.27) the partial potential in the vapour phase is given by

$$\mu_i^v = -kT\log\{l_i'(T)j_i''(T)kT/p_i\},$$

from which it follows that

$$\mu_i^v = \mu_{i,0}^v + kT\log\frac{p_i}{p_{i,0}}, \tag{1.28}$$

where the subscript 0 is used to indicate the pure species. For equilibrium it is necessary that the partial potentials in the two phases should be equal. It follows therefore that

$$\left.\begin{aligned} p_i &= p_{i,0}\frac{N_i}{N_i+N_j}, \\ p_j &= p_{j,0}\frac{N_j}{N_i+N_j}, \end{aligned}\right\} \tag{1.29}$$

which is Raoult's law. Equations (1.29) have been obtained by assuming that the energy of mixing is zero, without recourse to the more restrictive condition of negligible interactions between all pairs of molecules.

1.15. It has been shown that, in general, the configurational factor in the partition function for a strictly regular solution is given by

$$\Omega(T) = \frac{1}{N_i!\,N_j!}\int\cdots\int e^{\{N_i\chi_i+N_j\chi_j-Xw_{ij}\}/kT}(d\omega_i)^{N_i}(d\omega_j)^{N_j}. \tag{1.15}$$

The evaluation of the integral in equation (1.15) can be carried out only approximately. A quantity $\bar{\bar{X}}$ defined by the equation

$$e^{-\bar{\bar{X}}w_{ij}/kT}\int\cdots\int(d\omega_i)^{N_i}(d\omega_j)^{N_j} = \int\cdots\int e^{-Xw_{ij}/kT}(d\omega_i)^{N_i}(d\omega_j)^{N_j} \tag{1.30}$$

can be introduced. The integral in the left-hand member can be evaluated as in equation (1.16); this leads to the result

$$\Omega(T) = \left\{ev_i\exp\left(\frac{\chi_i}{kT}\right)\right\}^{N_i}\left\{ev_j\exp\left(\frac{\chi_j}{kT}\right)\right\}^{N_j}\frac{(N_i+N_j)!}{N_i!\,N_j!}\exp\left(-\frac{\bar{\bar{X}}w_{ij}}{kT}\right) \tag{1.31}$$

this was the device used by Guggenheim,[†] although he neglected to distinguish between $\overline{\overline{X}}$ defined by equation (1.30) and the average or equilibrium value $\bar{X}$. However, $\bar{X}$ and $\overline{\overline{X}}$ are not identical[‡] and the relation between them can be seen in the following way. By differentiating equation (1.30) with respect to T it can be shown that, provided w_{ij} is sensibly independent of T, then

$$\bar{X} = \overline{\overline{X}} - T\frac{\partial \overline{\overline{X}}}{\partial T} = \frac{\partial(\overline{\overline{X}}/T)}{\partial(1/T)}, \tag{1.32}$$

where $\bar{X}$ is the equilibrium value of X and is defined, in the usual way, by

$$\bar{X}\int\ldots\int \epsilon^{-Xw_{ij}/kT}(d\omega_i)^{N_i}(d\omega_j)^{N_j} = \int\ldots\int X\epsilon^{-Xw_{ij}/kT}(d\omega_i)^{N_i}(d\omega_j)^{N_j}. \tag{1.33}$$

Alternatively, in the light of what has been said in §§ 1.6 and 1.11, $\Omega(T)$ can be expressed formally as

$$\Omega(T) = g(N_i, N_j, X)\exp(-Xw_{ij}/kT)\{\epsilon v_i \exp(\chi_i/kT)\}^{N_i}\times$$
$$\times\{\epsilon v_j \exp(\chi_j/kT)\}^{N_j}, \tag{1.34}$$

where $g(N_i, N_j, X)$ is the number of distinguishable configurations of the N_i molecules i and N_j molecules j in which there are zX closest neighbour i—j contacts.

To proceed farther it is necessary, on the one hand, to evaluate $\bar{X}$ or $\overline{\overline{X}}$ or, on the other hand, to evaluate $g(N_i, N_j, X_{ij})$. No simple method is available, and it is necessary to fall back on approximate methods, the detailed consideration of which is deferred to a later stage (Chapters III and V). In fact, the difficulty in the evaluation of the configurational term in the partition function for a strictly regular solution has led to the kernel of the difficulty of the statistical mechanics of solutions of high polymers. For when the assembly contains particles of markedly different size, the combinatory factor, even when the energy of mixing is zero, contains parameters which involve pairs of sites and their interrelation, in a way similar, for example, to the parameters X of equations (1.15) and (1.34). Thus the determination of the partition function for mixtures containing polymer molecules, whether the energy of mixing be zero or not, involves problems of the same kind as that implicit in the evaluation of equations (1.15), (1.31), or (1.34). The nature and occasion of the essential difficulty will become clearer by considering solutions of long chain molecules in relation to the quasi-crystalline model of a liquid which has been adopted.

[†] Guggenheim, E. A., *Proc. Roy. Soc.* A **148** (1935), 304.

[‡] Rushbrooke, G. S., ibid. A **166** (1938), 296.

II

LONG CHAIN MOLECULES

2.1. THE quasi-crystalline model of a liquid which has been described in § 1.9 will be used. On the average there is a definite relationship between any molecule and its near neighbours which can be specified by a coordination number z, although the fluctuations about the average positions are sufficient to destroy any long-range order. From another point of view the whole liquid can be regarded as providing a potential field of which the minima provide an array of sites which can be occupied by the molecules of different kinds. There is a definite geometrical relationship between any site and its near neighbours which, on the average, is very similar to that in a crystal, but there is no long-range order. For a mixture in which the molecules of each kind are at least roughly spherical and of about the same size, each molecule of whatever kind can be regarded as occupying one site. The combinatory factor in the partition function arises from the number of arrangements of molecules of different kinds over the available sites for each value of the interaction energy. This is precisely what has been done in considering regular solutions in §§ 1.13 and 1.15. The task now is to examine the use of the quasi-crystalline model of a liquid when the molecules of one species are long chains.

2.2. First, consider a simple chain molecule which is formed by the repetition of a segment or sub-molecule. Any number of such substances can be called to mind; one which occurs naturally is rubber, in which the sub-molecule is an isoprene unit. If the whole molecule consists of r units ($r \gg 1$), then a suitable representation of it is to consider it to occupy r sites of the array in such a way that adjacent sub-molecules in the chain occupy closest neighbour sites. Each sub-molecule is regarded as occupying one site on the array, and this allows not only for the fact that a chain molecule is being considered but also permits a high degree of flexibility of each chain molecule. It is clear that, by the allocation of an appropriate number of sites, in which the sites which accommodate any pair of adjacent sub-molecules are suitably disposed, both branched chain and closed ring molecules can be discussed in terms of the quasi-crystalline model of a liquid. A physical representation of this sort also makes it possible to consider mixtures of species of which the volumes of the molecules differ in the ratio of small integers. For convenience and brevity, chain molecules which contain 2, 3, 4,..., r,... segments or sub-molecules will be referred to as dimer, trimer, tetramer..., r-mer,... molecules. In conformity with this convention, a simple molecule which can be accommodated on one site of the array will be called a monomer.

2.3. Consider a molecule which contains r units. The number of closest neighbour pairs of sites formed by the sites occupied by the r-mer and the rest of the sites† is denoted by zq. This quantity is the number of closest neighbour contacts or interactions into which the polymer molecule enters, for the definition excludes pairs of closest neighbour sites which are occupied by adjacent units of the polymer. We will now examine the value of zq for different kinds of polymer molecules.‡ For a simple chain molecule which contains r groups in all, there are $z-2$ closest neighbour interactions for each internal group and $z-1$ for each of the end groups. Thus there are

$$(r-2)(z-2)+2(z-1) = rz-2r+2$$

closest neighbour interactions in all. For a branched chain molecule there is one less interaction at the junction of each branch, but each branch introduces an additional end group and so an additional interaction. Thus the total number of interactions for a branched chain molecule is the same as for a simple chain molecule. In each case the parameter q has a value q' given by

$$(r-q')z = 2(r-1). \tag{2.1}$$

For a closed ring molecule this no longer holds. The essential fact can be expressed by saying that a closed ring molecule has no end groups: each group in a closed ring molecule gives rise to $z-2$ closest neighbour interactions. Thus for a closed ring molecule the parameter q has a value q'' given by

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† If the molecule coils back on itself so that two non-adjacent units of the molecule occupy a pair of closest neighbour sites, this pair should be included with regard to each of the sites.

‡ Miller, A. R., *Proc. Cambridge Phil. Soc.* **43** (1947), 422.

$$(r-q'')z = 2r. \tag{2.2}$$

It should be noted that for large r ($r \gg 1$) the values q' and q'' do not differ greatly. In the following paragraphs wherever the parameter q is used it is implied that it is to be given its appropriate value q' or q'' according to the type of molecule.

2.4. It will be useful at this stage to derive certain statistical relations which will be of frequent use. Consider a mixture which contains N_i molecules of species i (all i); each molecule of species i contains r_i segments and occupies r_i sites of the array in such a way that adjacent segments occupy closest neighbour sites. A parameter q_i is introduced for each species and is defined by the fact that each molecule i shares in zq_i closest neighbour interactions. The precise values of q_i are determined by equations (2.1) and (2.2), but are unimportant for the immediate purpose and play no part in the deduction of the results of this section.

Quantities X_{ij} (all i and j for which $i \neq j$) are defined so that zX_{ij} is the number of closest neighbour pairs of sites of which one is occupied by a molecule of species i and the other by a molecule of species j. Quantities X_{ii} (all i) can also be introduced and defined by the fact that zX_{ii} is the number of closest neighbour pairs of sites each of which is occupied by a molecule of species i including those closest neighbour pairs which (due to the molecule coiling back on itself) are occupied by non-adjacent units of the same molecule of species i but excluding those cases in which the pair of sites is occupied by adjacent units of the same molecule. A further quantity, x_{ii}, is defined as follows: let zx_{ii} (all i) be the number of pairs of sites which are occupied by two adjacent units of the same molecule of species i.

A molecule of species i shares in two kinds of closest neighbour interactions. It may give an interaction with another molecule i or with a non-adjacent sub-molecule of itself (forming an $i-i$ interaction in each case), or it may give an interaction

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with a molecule of another species (of which an i—j interaction is typical). In totalling all the interactions in which all the molecules of species i take part each of the former kind will be included twice and each of the latter kind will be included once. Hence

$$2X_{ii}+\sum_k{}' X_{ik} = q_i N_i \quad (\text{all } i). \tag{2.3}$$

Consider the r_i sites which accommodate a molecule of species i. Each site has z closest neighbours. The difference between zr_i and zq_i is simply twice the number of closest neighbour pairs which are occupied by adjacent sub-molecules of the same molecule i. Hence

$$2x_{ii}+2X_{ii}+\sum_k{}' X_{ik} = r_i N_i \quad (\text{all } i). \tag{2.4}$$

From equations (2.3) and (2.4) it follows that

$$2x_{ii} = (r_i-q_i)N_i \quad (\text{all } i) \tag{2.5}$$

for all types of molecules. It is an easy matter to express the quantities x_{ii} in terms of the r_i alone, but these expressions have different forms according to the kind of molecule; the virtue of equation (2.5) is that it gives a value for x_{ii} which is valid for closed ring molecules as well as for simple chain and branched chain molecules.

2.5. The configurational energy of the assembly is given by

$$W = z\sum_i X_{ii} V_{ii}+z\sum_{i<k} X_{ik} V_{ik},$$

where V_{ii}, V_{ik} are the average interaction energies due to closest neighbour i—i and i—k pairs respectively. This can be written as

$$W = \tfrac{1}{2}z\sum_i q_i N_i V_{ii}+\tfrac{1}{2}z\sum_{i<k} X_{ik}(2V_{ik}-V_{ii}-V_{kk}) \tag{2.6}$$

$$= -\sum_i q_i N_i \chi_i+\sum_{i<k} X_{ik} w_{ik}, \tag{2.7}$$

where w_{ik} are the energies of mixing of each pair of components, and are defined in equation (1.13), and $-\chi_i$ (all i) is the average potential energy of a molecule in the pure liquid i. The grand partition function of the assembly can then be written as

$$Z = \sum_{N_i}\sum_{X_{ij}} g(N_i, X_{ij})\exp\left\{\left(\sum_i q_i N_i \chi_i-\sum_{i<k} X_{ik} w_{ik}\right)\Big/kT\right\}\times$$

$$\times\prod_i \{ev_i l_i(T) j_i(T)\lambda_i\}^{N_i}, \tag{2.8}$$

where $g(N_i, X_{ij})$ is written for the number of ways of arranging N_i molecules of species i (all i) on the array of sites so that there are zX_{ij} closest neighbour contacts of the kind $i-j$ (all i, j); that is, $g(N_i, X_{ij})$ is the number of distinguishable arrangements of the assembly of N_i systems i (all i) with a specified configurational energy given by equation (2.7). If all the energies of mixing w_{ij} are zero, then the grand partition function is

$$Z = \sum_{N_i} g(N_i) \exp\left\{ \sum_i q_i N_i \chi_i / kT \right\} \prod_i \{\epsilon v_i l_i(T) j_i(T) \lambda_i\}^{N_i}, \qquad (2.9)$$

where $g(N_i)$ is the number of ways of arranging N_i systems i (all i) on the array of sites, independently of the numbers of closest neighbour contacts of different kinds, since now the configurational energy depends only on the numbers of systems of different kinds.

The essence of the determination of the grand partition function is to evaluate the combinatory factors $g(N_i)$ and $g(N_i, X_{ij})$. For the case of a mixture of roughly spherical molecules of about the same size with zero energies of mixing this is trivial, it is simply $\left(\sum_i N_i\right)! / \prod_i N_i!$. In all other cases its evaluation presents considerable difficulty and approximate methods must be used. The evaluation of $g(N_i, X_{ij})$ is equivalent to the evaluation of an integral such as that given in equation (1.15).

2.6. The nature of the difficulty can be seen from a consideration of a binary mixture of monomer molecules. From equation (2.3) it is clear that of the five quantities X_{ii}, X_{ij}, X_{jj}, N_i, and N_j which can be used to specify such a binary mixture only three are independent. Ordinarily, and as is implied by the way in which equation (2.8) has been written, different variables are used to enumerate the complexions of the assembly and to determine its configurational energy. Whereas the distinguishable configurations of the assembly are specified by the occupation of individual sites of the array, the configurational energy arises from closest neighbour (or more distant) interactions and has to be determined by the specification of closest neighbour (or more distant) pairs of sites. It therefore follows that if a means could be found by which both the evaluation of the configurational energy and the enumeration of the complexions of the assembly could be carried out in terms of one and the same kind of variable (that is, by the specification either of pairs of sites or of the occupation of individual sites, but not both), one could hope greatly to simplify the problem. The configurational energy can be expressed only in terms of the specification of pairs of sites; can, then, the distinguishable complexions of the assembly also be expressed in terms of these variables? The usual procedure is to take N_i, N_j, and X_{ij} as independent variables; the suggested procedure is to take X_{ii}, X_{jj}, and X_{ij} as independent variables. This possibility has been examined for a binary mixture of monomer molecules, in particular by Alfrey and Mark,† but it has been shown‡ that their treatment is based on an untenable assumption. Furthermore, such a specification introduces difficulties no less formidable than those which it was designed to overcome, so that its use must be abandoned. These difficulties had been previously recognized§ and an attempt had been made to introduce a correction for the interdependence of the distribution of pairs of sites of different kinds.

The nature of these difficulties can be seen from the following examination of the method used by Alfrey and Mark. They considered a set of $\frac{1}{2}N$ numbered pairs of closest neighbour lattice sites which are chosen in such a way that each site of the lattice belongs to one and to only one pair. If amongst the selected set of $\frac{1}{2}N$ closest neighbour pairs there are X i—j pairs, then the numbers of i—i and j—j pairs are $\frac{1}{2}(N_i-X)$ and $\frac{1}{2}(N_j-X)$ respectively. The number of configurations is then calculated by considering (i) the number of ways of arranging X indistinguishable elements of one kind, $\frac{1}{2}(N_i-X)$ indistinguishable elements of a second kind, and $\frac{1}{2}(N_j-X)$ indistinguishable elements of a third kind amongst the $\frac{1}{2}N$ available places, and (ii) by allowing for the fact that each i—j pair can be arranged in two distinct ways within its reference position. On this basis, they derive a combinatory factor

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† Alfrey, T., and Mark, H., *J. Chem. Phys.* **10** (1942), 303.

‡ Miller, A. R., ibid. **15** (1947), 513.

§ Fowler, R. H., and Guggenheim, E. A., *Proc. Roy. Soc.* A **174** (1940), 189, § 8.

$$\phi(X) = \frac{(\tfrac{1}{2}N)!\,2^X}{X!\,\{\tfrac{1}{2}(N_i-X)\}!\,\{\tfrac{1}{2}(N_j-X)\}!} \tag{2.10}$$

and, corresponding to this, a partition function

$$F = \sum_X \phi(X)\exp(-Xw_{ij}/kT), \tag{2.11}$$

apart from factors allowing for the internal motions of the molecules.

This treatment involves the assumption that if in the selected group of $\frac{1}{2}N$ closest neighbour pairs there are X pairs of the kind i—j, then in the complete assembly the total number of i—j pairs is exactly zX. It also implies that the total numbers of i—i and j—j pairs are $\frac{1}{2}z(N_i-X)$ and $\frac{1}{2}z(N_j-X)$ respectively. In fact, in terms of our notation, the assumption is

$$\left.\begin{aligned} zX &= zX_{ij}, \\ \tfrac{1}{2}z(N_i-X) &= zX_{ii} = \tfrac{1}{2}z(N_i-X_{ij}), \\ \tfrac{1}{2}z(N_j-X) &= zX_{jj} = \tfrac{1}{2}z(N_j-X_{ij}). \end{aligned}\right\} \tag{2.12}$$

This assumption is essential in the treatment given by Alfrey and Mark for two reasons: (i) In order that the interaction energy, which we have seen is equal to $X_{ij}w_{ij}$, can be expressed in terms of the parameter X which they introduce, namely, as Xw_{ij}. This is the specific form in which Alfrey and Mark express this assumption in equation (7) of their paper. (ii) It is also necessary because their treatment assumes that the particular arrangement of particles on the lattice in which there are zX_{ii}, zX_{ij}, and zX_{jj} pairs of i—i, i—j, and j—j closest neighbours respectively is equivalent to, and can be described precisely by, the allocation of X, $\frac{1}{2}(N_i-X)$, and $\frac{1}{2}(N_j-X)$ respectively i—j, i—i, and j—j pairs amongst the group of $\frac{1}{2}N$ pairs of sites selected in the way specified. This is considered further in the discussion below (equations (2.14) and (2.15)).

In fact, from a lattice of N sites in which no closest neighbours of any site are also closest neighbours of one another, a group of $\frac{1}{2}N$ closest neighbour pairs which are such that every lattice point belongs to one and to only one pair can be chosen in

$\{(z-1)^{z-1}/z^{z-2}\}^{\frac{1}{2}N}$ different ways.† While, at first sight, it appears possible that the assumption made by Alfrey and Mark might be valid (or nearly so) for a sufficient number of these possible selections of the group of pairs to enable the method to give a reasonable estimate of the combinatory factor, they offer no justification of it. Furthermore, it is difficult to discover any formal justification of their assumption. When the problem is examined from a somewhat different point of view, the nature and implications of the assumption made by Alfrey and Mark become clearer, and it is seen to be far from justified.

It has been noted above that X_{ii}, X_{ij}, and X_{jj} can be taken as the three independent parameters which are used to specify the assembly. With this specification the determination of the combinatory factor could then be regarded as a question of determining the number of ways in which zX_{ii} indistinguishable elements of one type, zX_{ij} indistinguishable elements of a second type, and zX_{jj} indistinguishable elements of a third type can be distributed amongst $\frac{1}{2}zN$ available pairs, *subject to any restrictions inherent in the interconnexions of the assembly.* The closing phrase indicates where the difficulty lies. A little reflection shows that if from the total number of available pairs, zX_{ii} are chosen for the $i—i$ closest neighbours, then not all the remaining $\frac{1}{2}z(N-X_{ii})$ pairs can be utilized to accommodate a $j—j$ pair, for it is inherent in the interconnexions of the pairs that a large number of those now remaining can accommodate only an $i—j$ pair. Furthermore, the position is not eased by selecting the pairs for the $i—j$ closest neighbour pairs second; for unless severe restrictions on our freedom of choice of the required number of pairs are accepted, we would be left finally with a large number of pairs which could not accommodate a $j—j$ closest neighbour pair and at the same time an insufficient number of possible pairs to accommodate all the $j—j$ closest neighbours. In passing it should also be noted that the precise specification of these restrictions, if not impossible, is certainly neither simple nor straightforward. It appears likely that it is in this restriction on the free choice of elements to accommodate the closest neighbour pairs of different kinds that the implications of the assumption made by Alfrey and Mark are to be found. We now proceed to show that this is, in fact, the case.

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† Miller, A. R., *Proc. Cambridge Phil. Soc.* **38** (1942), 109, equation (16).

Stirling's theorem for the asymptotic behaviour of a factorial ensures that for large values of r and s and a constant α we have

$$\alpha\log\frac{(r+s)!}{r!\,s!}=\log\frac{\{\alpha(r+s)\}!}{(\alpha r)!\,(\alpha s)!}. \tag{2.13}$$

If the assumption made by Alfrey and Mark, equation (2.12), can be justified, it then follows that

$$\left[\frac{(\frac{1}{2}N)!}{X!\,\{\frac{1}{2}(N_i-X)\}!\,\{\frac{1}{2}(N_j-X)\}!}\right]^z = \frac{(\frac{1}{2}zN)!}{(zX_{ij})!\,\{\frac{1}{2}z(N_i-X_{ij})\}!\,\{\frac{1}{2}z(N_j-X_{ij})\}!}. \tag{2.14}$$

The right-hand member of equation (2.14) reduces to

$$\frac{(\frac{1}{2}zN)!}{(zX_{ii})!\,(zX_{ij})!\,(zX_{jj})!}, \tag{2.15}$$

which is precisely the number of ways of arranging zX_{ii} elements of one kind, zX_{ij} elements of a second kind, and zX_{jj} elements of a third kind amongst $\frac{1}{2}zN$ positions *without any restriction whatsoever*. Thus the assumption made by Alfrey and Mark amounts to neglecting the restrictions on the allocation of the closest neighbour pairs of different kinds which are inherent in the arrangements of two or more species of molecules on a regular lattice. Thus it gives a value for the combinatory factor which is too large and far from correct.

When the molecules of one or more species of the mixture consist of chain molecules, the number of closest neighbour pairs occupied by adjacent sub-molecules must also be specified. These are the quantities x_{ii} defined by equation (2.5). In the general case the suggested procedure would be to take quantities of which X_{ii}, X_{ij}, and x_{ii} are representative as independent variables. Here there is also an interdependence between the x_{ii} pairs of closest neighbour sites which are occupied by adjacent segments of the polymer molecule. In short, the x_{ii} pairs have to be selected according to the sites which can accommodate one of the polymer molecules; and there is no simple way by which this constraint can be taken into account. It is a constraint of precisely the same kind as that implicit in the specification of the numbers of closest neighbour contacts of different kinds, which has been dealt with in detail in the preceding paragraphs. Furthermore, this difficulty persists for mixtures for which the energies of mixing are zero. We conclude that no simple distribution of pairs of sites of different kinds amongst the available pairs of sites on the array can provide a means of evaluating the combinatory factor in any of the cases of interest. Recourse must therefore be made to indirect methods of evaluating the relevant partition functions. We now proceed to examine these methods.

III

EVALUATION OF THE COMBINATORY FACTOR

3.1. To evaluate the partition function for a co-operative assembly we have seen that it is necessary to proceed by some indirect method. If the equilibrium properties of the assembly can be determined by an indirect method, then it will clearly be possible to evaluate the partition function, and, in particular, the combinatory factor by a process which is just the reverse of that normally used to determine the equilibrium properties from the partition function. The purpose of this chapter is to consider some of the methods which have been used to determine the free energy and the equilibrium properties of a co-operative assembly, and from them to determine the combinatory factor which occurs in the partition function for such an assembly. The treatment is confined to the scope of this monograph and is not intended as an exhaustive examination of the statistical mechanics of co-operative assemblies in general. Attention is focused on those methods which have proved most useful in the theory of solutions of high polymers.

The free energy of a co-operative assembly can be expanded formally as a power series[†] in $1/kT$, in which the coefficients of the successive terms are the cumulants of the unweighted average values of the moments of the configurational energy. In effect, this gives a power series expansion for the quantity $\bar{\bar{X}}$ defined in equation (1.30), and the moments have been evaluated as far as the third. In this way it can be shown that the approximation which had been used by Gorsky[‡] and by Bragg and Williams[§] in considering binary alloys was equivalent to neglecting all but the first term in the expansion, and that the method introduced by Bethe,[‖] in which local configurations are considered in detail, is valid up to the third moment of the configurational energy.[†] It has also been shown[‡] that to examine the properties of an extensive class of co-operative assemblies the method of chemical kinetics or the condition of quasi-chemical equilibrium[§] is equivalent to Bethe's method in its first approximation. Since an unambiguous formula for the combinatory factor, for a mixture containing polymer molecules with zero energy of mixing, was first obtained by using Bethe's approximation, we will now examine this approximation and its use in this connexion.

[†] Kirkwood, J. G., *J. Chem. Phys.* **6** (1938), 70.

[‡] Gorsky, W., *Zeit. f. Physik*, **50** (1928), 64.

[§] Bragg, W. L., and Williams, E. J., *Proc. Roy. Soc.* A **145** (1934), 669; ibid.

Bethe's method

3.2. In the Bragg–Williams approximation the evaluation of the integral in equation (1.15), or $\overline{\overline{X}}$ in equation (1.30), or of $g(N_i, X_{ij})$ in equation (2.8) is avoided by assuming that the force tending to produce order at a given point is determined uniquely by the average state of order throughout the assembly. Actually the order at a particular site of the array depends on the configuration of the particles in its immediate neighbourhood and only the average local configuration is determined by the long-range order of the array as a whole. There are fluctuations about this average configuration and corresponding fluctuations in the configurational energy. The neglect of these fluctuations simplified the problem by making a less precise specification of states of different configurational energy adequate. To take the fluctuations into account, it is necessary to determine $\overline{\overline{X}}$ or $g(N_i, X_{ij})$, as will have been evident from the considerations of §§ 1.15 and 2.5.

An approximate value of the partition function taking account of the local fluctuations can be obtained in the following way.[‖] It is simplest to outline the argument for a binary quasi-crystalline mixture of simple molecules. The occupation of a small group of sites is considered in detail. Suitable groups are one site, such as site 0 in Fig. 1, a pair of closest neighbour sites, such as sites 0 and 1 in Fig. 1, a central site and its first shell of z closest neighbour sites, such as sites 0, 1, 2, 3, 4 in Fig. 1, and so forth. In the first case the assembly consists of one site (the central site) and a residue which forms an external field of force so far as the central site is concerned; in the second it consists of a single pair of sites and a residue which provides an external field of force; in the next case the assembly consists of a central site and its closest neighbours ($z+1$ sites in all) in a field of force provided by the remaining $N-z-1$ sites; and likewise for larger groups. In considering a group of $z+1$ sites consisting of a central site and its first shell of closest neighbours we impose the further restriction† that no closest neighbours of a given site are also closest neighbours of one another. The effect of this assumption has been examined for regular solutions of simple molecules‡ and for solutions of polymer molecules.§ Close-packing of the molecules is found not to introduce any significant difference in the results. Accordingly, because the simpler algebra makes the nature of the processes clearer, this restriction will be retained in this exposition of the method. The inter-

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[†] Bethe, H. A., and Kirkwood, J. G., *J. Chem. Phys.* **7** (1939), 578.

[‡] Rushbrooke, G. S., *Proc. Roy. Soc.* A **166** (1938), 296; Guggenheim, E. A., ibid. A **169** (1938), 134; Fowler, R. H., and Guggenheim, E. A., ibid. A **174** (1940), 189.

[§] See § 5.3.

[‖] Bethe, H. A., *Proc. Roy. Soc.* A **150** (1935), 552.

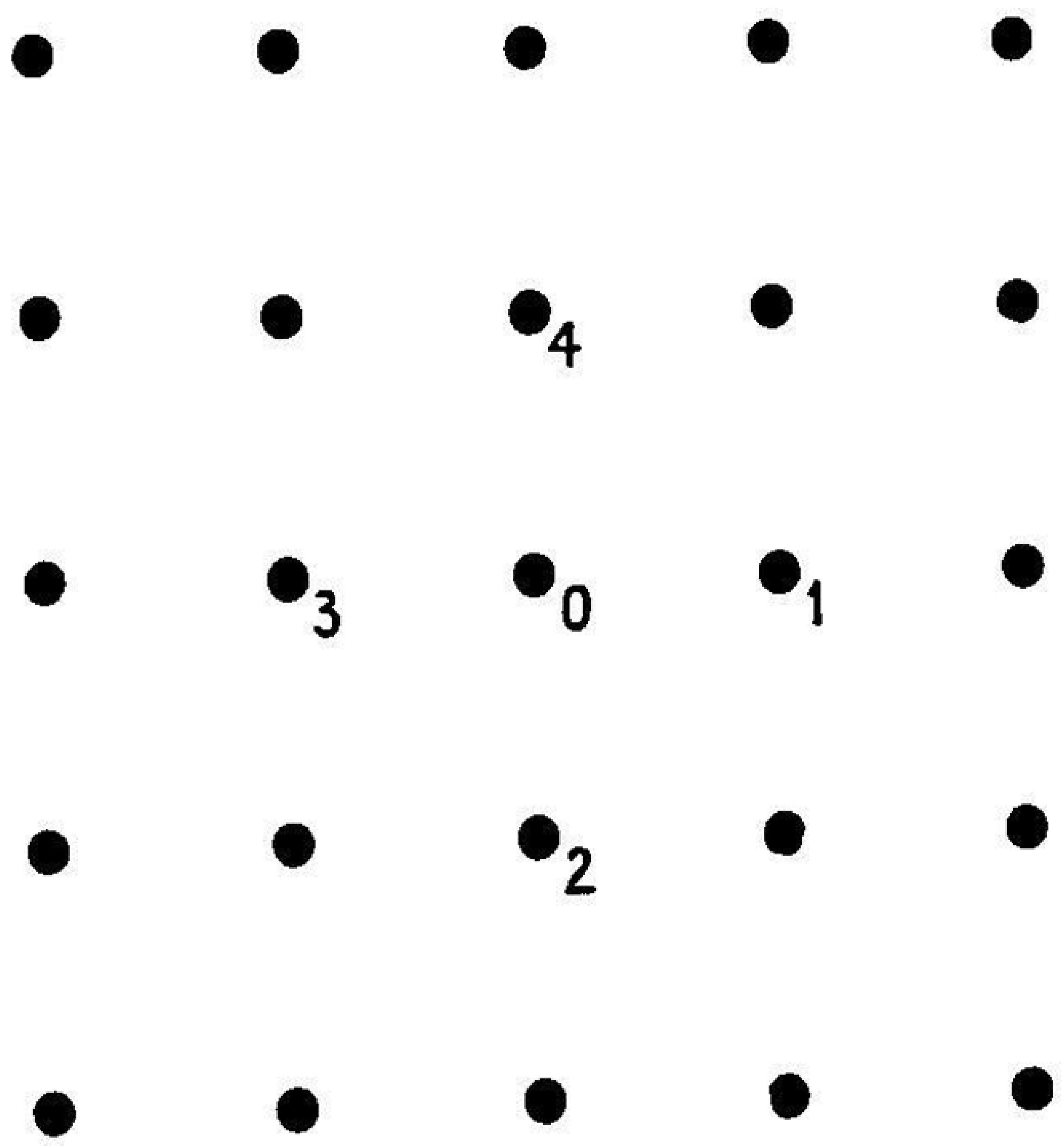

FIG. 1. Group of sites in applying Bethe's method (drawn for the two-dimensional case).

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† Cf. Bethe, H. A., *Proc. Roy. Soc.* A **150** (1935), 552.
‡ Rushbrooke, G. S., ibid. A **166** (1938), 296.

actions of the particles which occupy the selected group of sites are taken into account explicitly and equilibrium conditions are obtained by the requirement that both central and first shell sites must be average sites. Factors, ϵ, are used to specify the occupation of these sites in the following way: factors ϵ_i, ϵ'_i are introduced for each molecule of type i which occupies the central or a first shell site respectively; factors ϵ_j, ϵ'_j are introduced for each molecule of type j which occupies the central or a first shell site respectively. ϵ_i and ϵ_j are simply related to the corresponding absolute activities; ϵ'_i and ϵ'_j include in addition factors to take account of their interactions with particles in the residue of the assembly. The grand partition function is then given by

$$Z = \epsilon_i(\epsilon'_i+\eta\epsilon'_j)^z+\epsilon_j(\eta\epsilon'_i+\epsilon'_j)^z, \tag{3.1}$$

where η is written for $\exp(-w_{ij}/zkT)$ with w_{ij} (as before) the energy of mixing.

3.3. Some light is thrown on the nature of Bethe's method by a variant of it proposed by Guggenheim.† The grand partition function for a binary mixture is (cf. § 2.5)

$$Z = \sum_{N_i,N_j}\sum_{X_{ij}} g(N_i, N_j, X_{ij})\exp(-X_{ij}\,w_{ij}/kT)(\lambda_i\phi_i)^{N_i}(\lambda_j\phi_j)^{N_j}, \tag{3.2}$$

where the partition function of a molecule of type i for all degrees of freedom and all forms of energy other than the interaction energy has been denoted by ϕ_i. Thus

$$Z = \sum_{N_i,N_j} g(N_i, N_j, X_{ij})\eta_{ij}^{zX_{ij}}\xi_i^{N_i}\xi_j^{N_j}, \tag{3.3}$$

where η_{ij} has been written for $\exp(-w_{ij}/zkT)$ and ξ_i, ξ_j for $\lambda_i\phi_i$, $\lambda_j\phi_j$ respectively.

In equation (3.3) the series for Z can be replaced by its maximum term without introducing other than negligible errors in deriving averages. If the values of N_i, N_j, and X_{ij} in the maximum term be denoted by asterisks, then for the mean values we have

$$\bar{N}_i = N_i^*, \quad \bar{N}_j = N_j^*, \quad \bar{X}_{ij} = X^*, \tag{3.4}$$

and

$$Z = Z^* = g(N_i^*, N_j^*, X^*)\eta_{ij}^{zX^*}\xi_i^{N_i^*}\xi_j^{N_j^*}. \tag{3.5}$$

Now define geometrical means in the following way. Introduce a quantity ξ which is the geometrical mean of the factors of the type ξ_i contributed by each site of the array to Z^*; a quantity η which is the geometrical mean of the factors of the type η_{ij} contributed to Z^* by each pair of closest neighbour sites; a quantity γ which is the geometrical mean contribution per site to $g(N_i^*, N_j^*, X^*)$, and quantities typified by η_i which is the geometrical mean of the factors η_{ij} contributed to Z^* by each pair of closest neighbour sites of which one (at least) is specified as being occupied by a molecule of type i. Thus

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† Guggenheim, E. A., ibid. A **169** (1938), 134.

$$\left.\begin{aligned} \xi^N &= \xi_i^{N_i^*}\xi_j^{N_j^*}, \\ \eta^{\frac{1}{2}zN} &= \eta_{ij}^{zX^*}, \\ \gamma^N &= g(N_i^*, N_j^*, X^*). \end{aligned}\right\} \tag{3.6}$$

Now consider a central site and its z closest neighbours, and write down the terms contributed to Z^* by these $z+1$ sites explicitly and use the averages given by equations (3.6) for the contributions to Z^* made by the $N-z-1$ sites forming the residue of the assembly. This gives

$$\begin{aligned} Z^* = {} & [\xi_i(\xi_i\eta_i^{z-1}+\eta_{ij}\eta_j^{z-1}\xi_j)^z+\xi_j(\eta_{ij}\eta_i^{z-1}\xi_i+\eta_j^{z-1}\xi_j)^z]\times \\ & \times\gamma^{N-z-1}\xi^{N-z-1}\eta^{\frac{1}{2}zN-z^2}, \end{aligned} \tag{3.7}$$

where the factors of the type η_i^{z-1} are introduced to allow for the interactions between particles which occupy first shell sites and the outer sites. The exponent of the factors of the type η_i is necessarily $z-1$ since of the z closest neighbour interactions enjoyed by each particle which occupies a first shell site one, that with the central site, is introduced explicitly through the factors η_{ij}.

Now, if we write

$$\left.\begin{aligned} \xi_i &= \epsilon_i, \\ \xi_j &= \epsilon_j, \\ \xi_i\eta_i^{z-1} &= \epsilon_i', \\ \xi_j\eta_j^{z-1} &= \epsilon_j', \end{aligned}\right\} \tag{3.8}$$

we obtain

$$Z^* = \{\epsilon_i(\epsilon_i'+\eta_{ij}\epsilon_j')^z+\epsilon_j(\eta_{ij}\epsilon_i'+\epsilon_j')^z\}\gamma^{N-z-1}\xi^{N-z-1}\eta^{\frac{1}{2}zN-z^2}. \tag{3.9}$$

Since we are concerned with ratios of the terms in equation (3.9), which give the relative probabilities of different configurations it is clear that the common factor $\gamma^{N-z-1}\xi^{N-z-1}\eta^{\frac{1}{2}zN-z^2}$ can b omitted without possibility of error. This factor merely gives an average contribution from all sites other than the $z+1$ sites in the selected group. Thus correct results will be obtained by writing

$$Z = \epsilon_i(\epsilon_i'+\eta_{ij}\,\epsilon_j')^z+\epsilon_j(\eta_{ij}\,\epsilon_i'+\epsilon_j')^z \tag{3.10}$$

for the partition function. This is precisely the expression which is obtained† by constructing the grand partition function according to the method which was proposed by Bethe. The identity of equations (3.1) and (3.10) indicates the nature of Bethe's approximation and the physical significance of the ϵ factors. It requires no elaboration to establish that for a binary mixture it is only necessary to introduce ϵ factors for one of the two types of molecules, for the significant result will be the value of the ratio ϵ_i/ϵ_j and not the individual values of ϵ_i and ϵ_j. Generally, however, in the sequel we shall be concerned with the ratio of the ϵ_i, ϵ_j to the 'ϵ-factor' appropriate to a vacant site. As will be seen below, admitting the possibility of unoccupied sites provides a check on the internal consistency of the method.‡ The way is now clear to present the discussion of mixtures containing dimer and trimer molecules§ which led to the formulation of an expression for the combinatory factor appropriate to mixtures containing polymer molecules containing any number of segments.

Mixtures containing dimer molecules

3.4. A mixture of N_1 monomer and N_2 dimer molecules which can be arranged on a quasi-crystalline array of sites is considered. There are N sites in all, and

$$N = N_1+2N_2+N_v,$$

where N_v is the number of sites left vacant when all the monomer and dimer molecules have been arranged on the array of sites. The occupation of a group of sites consisting of a central site and its z closest neighbours (none of which is a closest neighbour of any other) will be examined in detail. The fractions of the total number of sites which are occupied by monomer and dimer molecules respectively will be denoted by θ_1 and θ_2, so that

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† Equation (3.1) above.

‡ Miller, A. R., *Proc. Cambridge Phil. Soc.* **42** (1946), 303.

§ Miller, A. R., ibid. **38** (1942), 109; ibid. **39** (1943), 54.

$$N_r = N(1-\theta_1-\theta_2).$$

In applying Bethe's method the parameters will be defined in the following way. For a monomer, ϵ_1 and ϵ_1' will be introduced according as it occupies the central or a first shell site. For a dimer which occupies the central site and a first shell site a parameter ϵ_2 will be introduced, and for a dimer which occupies a first shell site and an outer site a parameter ϵ_2'. It is worth while to consider this case in somewhat greater detail than will be necessary in considering other cases subsequently. Let the number of monomer and dimer molecules occupying the central site be denoted by $n_{1,0}$ and $n_{2,0}$ respectively; each of these can assume the values zero and unity, but if either is unity the other is necessarily zero. Further, let the numbers of monomer and dimer molecules which occupy first shell sites be denoted by $n_{1,1}$ and $n_{2,1}$ respectively. The weight factor, that is, the number of distinct ways in which a particular configuration specified by a given set of values of $n_{1,0}$, $n_{2,0}$, $n_{1,1}$, and $n_{2,1}$ can arise, will be denoted by g. All the ways in which the group of sites consisting of the central site and its closest neighbours can be occupied are indicated in Table 1, which for the sake of clarity is given for the case in which $z = 4$. Appropriate tables for other values of z can be constructed in a similar way. For instance, when $n_{1,0}$ is zero and $n_{2,0}$ is unity, the sum of $n_{1,1}$ and $n_{2,1}$ cannot exceed $z-1$; $n_{1,1}$ can be given the set of values $0, 1, 2,..., z-1$; if $n_{1,1}$ has the value r $(0 \leqslant r \leqslant z-1)$, then $n_{2,1}$ can assume the set of values $0, 1, 2,..., z-r-1$. The number of distinct arrangements in which the set of particular values

$$n_{1,0} = 0, \qquad n_{2,0} = 1, \qquad n_{1,1} = r_1, \qquad n_{2,1} = r_2,$$

where $0 \leqslant r_1 \leqslant z-1$, $0 \leqslant r_2 \leqslant z-r_1-1$, can arise is given by

$$g = z\binom{z-1}{r_1}\binom{z-r_1-1}{r_2}.$$

The corresponding weight factors and range of allowable values of $n_{1,1}$ and $n_{2,1}$ can be determined in a similar way for the other values of $n_{1,0}$ and $n_{2,0}$.

TABLE 1

Occupation of the group of $z+1$ *sites*

(*a*) $n_{1,0}$ zero, $n_{2,0}$ unity.

$n_{1,1}$	3	2	2	1	1	1	0	0	0	0
$n_{2,1}$	0	0	1	0	1	2	0	1	2	3
g	4	12	12	12	24	12	4	12	24	4

(*b*) $n_{1,0}$ zero, $n_{2,0}$ zero and (*c*) $n_{1,0}$ unity, $n_{2,0}$ zero.

$n_{1,1}$	4	3	3	2	2	2	1	1	1	1	0	0	0	0	0
$n_{2,1}$	0	1	0	2	1	0	3	2	1	0	4	3	2	1	0
g	1	4	4	6	12	6	4	12	12	4	1	4	6	4	1

The typical term in the grand partition function constructed according to Bethe's method is

$$g\epsilon_1^{n_{1,0}}\epsilon_2^{n_{2,0}}\epsilon_1'^{n_{1,1}}\epsilon_2'^{n_{2,1}}\eta^{n_{1,0}n_{2,1}+n_{2,0}n_{1,1}}.$$

Here η has been written for $\exp(-w_{12}/zkT)$, where w_{12} is the energy of mixing of monomer and dimer molecules, and the energy zero is chosen so that the total interaction energy of the pure species is zero. This term gives the relative probability of that mode of occupation of the group of sites which is specified by the given set of values of $n_{1,0}$, $n_{2,0}$, $n_{1,1}$, and $n_{2,1}$. It therefore follows that if the partition function is constructed according to Bethe's method we get†

$$Z = (1+\epsilon_1'+\epsilon_2')^z+\epsilon_1(1+\epsilon_1'+\eta\epsilon_2')^z+z\epsilon_2(1+\eta\epsilon_1'+\epsilon_2')^{z-1}. \quad (3.11)$$

3.5. The frequencies of occupation of the central site by monomer and dimer molecules respectively are given by $\epsilon_1\,\partial\log Z/\partial\epsilon_1$ and $\epsilon_2\,\partial\log Z/\partial\epsilon_2$. Since the central site is chosen at random its frequency of occupation by different molecules must be the ne as that of any other site, that is, it is an average site, ence

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† The corresponding result for the two-dimensional problem of an adsorbed monolayer was given by Roberts, J. K., and Miller, A. R., *Proc. Cambridge Phil. Soc.* **35** (1939), 293, and by Chang, T. S., *Proc. Roy. Soc.* A **169** (1939), 512, and for a three-dimensional array of sites, all of which are occupied, by Miller, A. R., *Proc. Cambridge Phil. Soc.* **38** (1942), 109. It should be noted that the treatment given by Chang in § 3 of his paper is open to objection, as is also

$$\frac{\theta_1}{1-\theta_1-\theta_2} = \frac{\epsilon_1(1+\epsilon_1'+\eta\epsilon_2')^z}{(1+\epsilon_1'+\epsilon_2')^z}, \tag{3.12}$$

$$\frac{\theta_2}{1-\theta_1-\theta_2} = \frac{z\epsilon_2(1+\eta\epsilon_1'+\epsilon_2')^{z-1}}{(1+\epsilon_1'+\epsilon_2')^z}. \tag{3.13}$$

nen the central site is unoccupied, the average numbers of t shell sites which are occupied by monomer and dimer molecules respectively are given by $\epsilon_1' \partial \log Z_0/\partial\epsilon_1'$ and $\epsilon_2' \partial \log Z_0/\partial\epsilon_2'$, ere Z_0 has been written for the first term in the right-hand mber of equation (3.11). When the central site is occupied by nonomer, the average numbers of first shell sites which are cupied by monomer and dimer molecules respectively are ven by $\epsilon_1' \partial \log Z_1/\partial\epsilon_1'$ and $\epsilon_2' \partial \log Z_1/\partial\epsilon_2'$, where Z_1 has been itten for the second term in the right-hand member of equation .11). Likewise, when the central site is occupied by a dimer, e average numbers of first shell sites which are occupied monomer and dimer molecules respectively are given by $\partial \log Z_2/\partial\epsilon_1'$ and $1+\epsilon_2' \partial \log Z_2/\partial\epsilon_2'$, where Z_2 has been written for e third term of the right-hand member of equation (3.11). nce the first shell sites are average sites their overall average cupation by monomer and dimer molecules respectively must $z\theta_1$ and $z\theta_2$. Thus

$$z\theta_1 = (1-\theta_1-\theta_2)\epsilon_1'\frac{\partial \log Z_0}{\partial\epsilon_1'} + \theta_1\epsilon_1'\frac{\partial \log Z_1}{\partial\epsilon_1'} + \theta_2\epsilon_1'\frac{\partial \log Z_1}{\partial\epsilon_1'}, \tag{3.14}$$

$$z\theta_2 = (1-\theta_1-\theta_2)\epsilon_1'\frac{\partial \log Z_0}{\partial\epsilon_2'} + \theta_1\epsilon_2'\frac{\partial \log Z_1}{\partial\epsilon_2'} + \theta_2\left(1+\epsilon_2'\frac{\partial \log Z_2}{\partial\epsilon_2'}\right). \tag{3.15}$$

3.6. For the case in which the energy of mixing is zero, quations (3.12) and (3.13) reduce to

$$\frac{\theta_1}{1-\theta_1-\theta_2} = \epsilon_1, \tag{3.16}$$

In this case also, equations (3.14) and (3.15) give

$$z\theta_1(1+\epsilon_1'+\epsilon_2') = (z-\theta_2)\epsilon_1', \qquad \text{(3.1}$$

$$z\theta_2(1+\epsilon_1'+\epsilon_2') = \theta_2(1+\epsilon_1')+z\epsilon_2'. \qquad \text{(3.1}$$

The average number of vacant first shell sites is given by

$$z(1-\theta_1-\theta_2) = (1-\theta_1-\theta_2)\frac{z}{1+\epsilon_1'+\epsilon_2'}+$$

$$+\theta_1\frac{z}{1+\epsilon_1'+\epsilon_2'}+\theta_2\frac{z-1}{1+\epsilon_1'+\epsilon_2'},$$

whence $$z(1-\theta_1-\theta_2)(1+\epsilon_1'+\epsilon_2') = z-\theta_2. \qquad \text{(3.2}$$

By adding equations (3.18) and (3.19) and subtracting the su from $z(1+\epsilon_1'+\epsilon_2')$ equation (3.20) is recovered as is necessar Substituting the value of $1+\epsilon_1'+\epsilon_2'$ given by equation (3.20) i equation (3.17) we obtain

$$\epsilon_2 = \frac{\theta_2(z-\theta_2)}{z^2(1-\theta_1-\theta_2)^2}. \qquad \text{(3.2}$$

Equations (3.16) and (3.21) give the essential results for o immediate purpose.

Partial differential equations for the combinatory factor

3.7. It has been seen (§ 3.3) that the parameters ϵ_i which a introduced in Bethe's method have to be identified with which is the product of the absolute activity λ_i and the partitic function ϕ_i for all degrees of freedom and all forms of energ other than the interaction energy. The relation between the and the combinatory factor can be found by considering t grand partition function. For a mixture of any number of speci it can be written in the form

$$Z = \sum_{N_i}\sum_{X_{ij}} g(N_i, X_{ij}) \prod_{N_i} \xi_i^{N_i} \prod_{X_{ij}} \eta_{ij}^{zX_{ij}}, \qquad \text{(3.2}$$

where the notation is the same as that used hitherto. Since th series can be replaced by its maximum term with only negl uilibrium values $\overline{N}_i, \overline{X}_{ij}$ of the N_i and the X_{ij} are given by the s of equations

$$\frac{\partial}{\partial N_i}\log g(N_i, X_{ij})+\log \xi_i = 0 \quad (\text{all } i), \tag{3.23}$$

$$\frac{\partial}{\partial X_{ij}}\log g(N_i, X_{ij})+z\log \eta_{ij} = 0 \quad (\text{all } i, j). \tag{3.24}$$

order to obtain an expression for the combinatory factor it is sumed that the equilibrium conditions determined by Bethe's ethod are precisely equivalent to those determined by the sets equations (3.23) and (3.24). That is, that the θ_i (determined equations such as (3.16) and (3.21)), which give the average actions of the total number of sites which are occupied in a ecified manner, and the N_i determined by equations (3.23) d (3.24) give identical specifications of the equilibrium state. ius

$$N\theta_i = r_i \overline{N}_i,$$

iere r_i is the number of sites which are occupied by each molele i.

For the case in which the energies of mixing are zero there is nply a set of equations corresponding to (3.23). Identifying e ξ_i with the ϵ_i of Bethe's method and writing the equations terms of the θ_i rather than in terms of the N_i, these give, in neral, for a mixture of two species of molecules,

$$\left.\begin{aligned} \frac{r_i}{N}\frac{\partial}{\partial\theta_i}\log g(N_i, N_j, N_v)+\log \epsilon_i &= 0, \\ \frac{r_j}{N}\frac{\partial}{\partial\theta_j}\log g(N_i, N_j, N_v)+\log \epsilon_j &= 0. \end{aligned}\right\} \tag{3.25}$$

ı order that these partial differential equations shall be ingrable it is necessary that

$$r_j\frac{\partial}{\partial\theta_j}\log \epsilon_i = r_i\frac{\partial}{\partial\theta_i}\log \epsilon_j, \tag{3.26}$$

nd the integrability of the partial differential equations proides a check on the internal consistency and the validity of ethe's approximation †

Combinatory factor for a mixture containing dimer molecules

3.8. From the values given for ϵ_1 and ϵ_2 by equations (3.16 and (3.21) it can be verified that

$$2\frac{\partial}{\partial\theta_2}\log\epsilon_1 = 2(1-\theta_1-\theta_2)^{-1} = \frac{\partial}{\partial\theta_1}\log\epsilon_2.$$

Thus the partial differential equations

$$\frac{1}{N}\frac{\partial}{\partial\theta_1}\log g(N_1,N_2,N_v)+\log\theta_1-\log(1-\theta_1-\theta_2) = 0,$$

$$\frac{2}{N}\frac{\partial}{\partial\theta_2}\log g(N_1,N_2,N_v)+\log\theta_2+\log(z-\theta_2)-2\log(1-\theta_1-\theta_2)-$$
$$-2\log z =$$

are integrable; and integrating them the combinatory facto $g(N_1,N_2,N_v)$ can be evaluated. The constant of integration i determined by the fact that when N_2 is zero, $g(N_1,N_2,N_v)$ mus reduce to the number of ways of arranging N_1 indistinguishabl particles on N_1+N_v sites leaving N_v sites vacant, that is, by th fact that

$$g(N_1,0,N_v) = (N_1+N_v)!/N_1!\,N_v!.$$

Integrating the above partial differential equations we obtain

$$\log g(N_1,N_2,N_v) = -\theta_1\log\theta_1-\tfrac{1}{2}\theta_2\log\theta_2+\tfrac{1}{2}(z-\theta_2)\log(z-\theta_2)-$$
$$-(1-\theta_1-\theta_2)\log(1-\theta_1-\theta_2)+\theta_2\log z-\tfrac{1}{2}z\log z. \quad (3.2$$

If θ_1 and θ_2 are replaced by their values in terms of N_1, N_2, an N_v we obtain finally

$$g(N_1,N_2,N_v) = \left[\frac{\{N_1+2(z-1)N_2/z+N_v\}!}{(N_1+2N_2+N_v)!}\right]^{\frac{1}{2}z}\frac{(N_1+2N_2+N_v)!}{N_1!\,N_2!\,N_v!}\left(\frac{z}{\sigma}\right)^{N} \quad (3.2$$

where σ is the symmetry number for the dimer molecules and equal to 2 if the ends of the molecule are indistinguishable, an to unity otherwise.

Mixtures containing trimer molecules

3.9. A mixture of N_1 monomer and N_3 trimer molecules whic can be arranged on a quasi-crystalline array of sites is considere There are N sites in all, and where N_v is the number of sites left vacant when all the monomer and trimer molecules have been arranged on the array of sites. As in the case of the mixture containing dimer molecules, the occupation of a group of sites consisting of a central site and its first shell of z closest neighbours is examined in detail. The fractions of the total number of sites which are occupied by monomer and trimer molecules respectively will be denoted by θ_1 and θ_3. The Bethe ϵ-parameters will be defined in the following way. For a trimer which has its centre sub-molecule on the central site of the group a parameter ϵ_3 will be introduced; for a trimer which has an end sub-molecule on the central site of the group a parameter ϵ_3' will be used, and for a trimer which has an end sub-molecule on a first shell site and its other sub-molecules on outer sites a parameter ϵ_3'' will be used. Parameters ϵ_1, ϵ_1' will be introduced for the monomer molecules according as they occupy the central or a first shell site. The detailed occupation of the selected group of sites can be considered in exactly the same way as was done in § 3.4 for mixtures containing dimer molecules. When the energy of mixing is zero, Bethe's approximate grand partition function is

$$\begin{aligned} Z = {} & (1+\epsilon_1'+\epsilon_3'')^z+\epsilon_1(1+\epsilon_1'+\epsilon_3'')^z+z\epsilon_3'(1+\epsilon_1'+\epsilon_3'')^{z-1}+ \\ & \qquad\qquad +\tfrac{1}{2}z\epsilon_3(1+\epsilon_1'+\epsilon_3'')^{z-2} \qquad (3.29) \\ \equiv {} & \quad Z_0 \quad + \quad Z_1 \quad + \quad Z_2 \quad + \quad Z_3, \end{aligned}$$

which serves to define the quantities Z_0, Z_1, Z_2, and Z_3 which are introduced for convenience of notation. Equation (3.29) is the grand partition function for the case in which the trimer molecules are completely inflexible. The case of perfectly flexible molecules can also be considered without difficulty, for the only difference is that the numerical factor $\frac{1}{2}z$ in the quantity Z_3 must be replaced by $\frac{1}{2}z(z-1)$. This makes no significant difference in the analysis.

3.10. The frequencies of occupation of the central site by monomer and trimer molecules respectively are given by $\epsilon_1\,\partial\log Z/\partial\epsilon_1$ and $\epsilon_3\,\partial\log Z/\partial\epsilon_3+\epsilon_3'\,\partial\log Z/\partial\epsilon_3'$. Since the average mode of occupation of the central site must be the same as that of any other site it follows that

$$\frac{\theta_1}{1-\theta_1-\theta_3} = \epsilon_1 \tag{3.30}$$

and

$$\frac{\theta_3}{1-\theta_1-\theta_3} = \frac{z\epsilon_3'(1+\epsilon_1'+\epsilon_3'')+\tfrac{1}{2}z\epsilon_3}{(1+\epsilon_1'+\epsilon_3'')^2}. \tag{3.31}$$

In those configurations in which any given site is occupied by a trimer molecule it must be occupied by an end segment in twice as many configurations as it is occupied by the centre segment of a trimer. Applying this to the occupation of the central site of the group it follows that

$$2\epsilon_3\frac{\partial}{\partial\epsilon_3}\log Z = \epsilon_3'\frac{\partial}{\partial\epsilon_3'}\log Z,$$

whence

$$\epsilon_3 = \epsilon_3'(1+\epsilon_1'+\epsilon_3''). \tag{3.32}$$

Now consider the occupation of the first shell sites by monomer and trimer molecules. Considering separately the occupation of the first shell sites according to the mode of occupation of the central site, in the same way as was done in the case of a mixture containing dimer molecules, it follows that the frequencies of occupation of the first shell sites by monomer and trimer molecules respectively are given by

$$(1-\theta_1-\theta_3)\epsilon_1'\frac{\partial\log Z_0}{\partial\epsilon_1'}+\theta_1\,\epsilon_1'\frac{\partial\log Z_1}{\partial\epsilon_1'}+\tfrac{2}{3}\theta_3\,\epsilon_1'\frac{\partial\log Z_2}{\partial\epsilon_1'}+$$

$$+\tfrac{1}{3}\theta_3\,\epsilon_1'\frac{\partial\log Z_3}{\partial\epsilon_1'}$$

and

$$(1-\theta_1-\theta_3)\epsilon_3''\frac{\partial\log Z_0}{\partial\epsilon_3''}+\theta_1\,\epsilon_3''\frac{\partial\log Z_1}{\partial\epsilon_3''}+\tfrac{2}{3}\theta_3\left(1+\epsilon_3''\frac{\partial\log Z_2}{\partial\epsilon_3''}\right)+$$

$$+\tfrac{1}{3}\theta_3\left(2+\epsilon_3''\frac{\partial\log Z_3}{\partial\epsilon_3''}\right).$$

These expressions have the values

$$(1-\theta_1-\theta_3)\frac{z\epsilon_1'}{1+\epsilon_1'+\epsilon_3''}+\theta_1\frac{z\epsilon_1'}{1+\epsilon_1'+\epsilon_3''}+\tfrac{2}{3}\theta_3\frac{(z-1)\epsilon_1'}{1+\epsilon_1'+\epsilon_3''}+$$

$$+\tfrac{1}{3}\theta_3\frac{(z-2)\epsilon_1'}{} \qquad (3.33)$$

and

$$(1-\theta_1-\theta_3)\frac{z\epsilon_3''}{1+\epsilon_1'+\epsilon_3''}+\theta_1\frac{z\epsilon_3''}{1+\epsilon_1'+\epsilon_3''}+\tfrac{2}{3}\theta_3\left(1+\frac{(z-1)\epsilon_3''}{1+\epsilon_1'+\epsilon_3''}\right)+$$
$$+\tfrac{1}{3}\theta_3\left(2+\frac{(z-2)\epsilon_3''}{1+\epsilon_1'+\epsilon_3''}\right). \quad (3.34)$$

Since the first shell sites are average sites, expressions (3.33) and (3.34) must be equal to $z\theta_1$ and $z\theta_3$ respectively. This leads to the equations

$$z\theta_1(1+\epsilon_1'+\epsilon_3'') = z\epsilon_3''+\tfrac{4}{3}(1+\epsilon_1')\theta_3 \quad (3.35)$$

and

$$z\theta_3(1+\epsilon_1'+\epsilon_3'') = z\epsilon_1'-\tfrac{4}{3}\epsilon_1'\,\theta_3. \quad (3.36)$$

By analogy with expressions (3.33) and (3.34) the number of vacant first shell sites must be given formally by

$$(1-\theta_1-\theta_3)\frac{z}{1+\epsilon_1'+\epsilon_3''}+\theta_1\frac{z}{1+\epsilon_1'+\epsilon_3''}+\tfrac{2}{3}\theta_3\frac{z-1}{1+\epsilon_1'+\epsilon_3''}+$$
$$+\tfrac{1}{3}\theta_3\frac{z-2}{1+\epsilon_1'+\epsilon_3''},$$

which leads to the equation

$$z(1-\theta_1-\theta_3)(1+\epsilon_1'+\epsilon_3'') = z-\tfrac{4}{3}\theta_3. \quad (3.37)$$

If we add equations (3.35) and (3.36) and subtract the sum from $z(1+\epsilon_1'+\epsilon_3'')$ we recover equation (3.37) as is necessary. Equations (3.31), (3.32), and (3.37) can be solved for ϵ_3 and we obtain

$$\epsilon_3 = \frac{2}{z^3}\frac{\theta_3(z-\frac{4}{3}\theta_3)^2}{(1-\theta_1-\theta_3)^3}. \quad (3.38)$$

The partial differential equations for $g(N_1, N_3, N_v)$ are therefore

$$\frac{1}{N}\frac{\partial}{\partial\theta_1}\log g(N_1, N_3, N_v)+\log\theta_1-\log(1-\theta_1-\theta_3) = 0,$$

$$\frac{3}{N}\frac{\partial}{\partial\theta_3}\log g(N_1, N_3, N_v)+\log\theta_3+2\log(z-\tfrac{4}{3}\theta_3)-3\log(1-\theta_1-\theta_3)+$$
$$+\log\frac{2}{3z^3} = 0. \quad (3.39)$$

From the values given for ϵ_1 and ϵ_3 by equations (3.30) and (3.38) it can be verified that

$$3\frac{\partial}{\partial\theta_1}\log\epsilon_1 = 3(1-\theta_1-\theta_3)^{-1} = \frac{\partial}{\partial\theta_3}\log\epsilon_3.$$

Thus the partial differential equations (3.39) are integrable. Integrating them we obtain

$$\begin{aligned}\frac{1}{N}\log g(N_1, N_3, N_v) &= -\theta_1 \log \theta_1 - \tfrac{1}{3}\theta_3 \log \theta_3 - (1-\theta_1-\theta_3)\log(1-\theta_1-\theta_3) + \\ &\quad + \tfrac{1}{2}(z-\tfrac{4}{3}\theta_3)\log(z-\tfrac{4}{3}\theta_3) + \tfrac{1}{3}\theta_3 \log\frac{3z^3}{2} - \tfrac{1}{2}z\log z, \qquad (3.40)\end{aligned}$$

where the constant of integration has been determined by the fact that when θ_3 (that is, N_3) is zero $g(N_1, N_3, N_v)$ must reduce to $(N_1+N_v)!/N_1!\,N_v!$. If θ_1 and θ_3 are replaced by their values in terms of N_1, N_3, and N_v we obtain finally

$$g(N_1, N_3, N_v) = \left[\frac{\{N_1+(3z-4)N_3/z+N_v\}!}{(N_1+3N_3+N_v)!}\right]^{\frac{1}{2}z} \frac{(N_1+3N_3+N_v)!}{N_1!\,N_3!\,N_v!}\left(\frac{z}{\sigma}\right)^{N_3}, \qquad (3.41)$$

where σ is the symmetry number for the trimer molecules. Equation (3.41) applies to completely inflexible molecules, that is, each trimer molecule is constrained to occupy a linear group of sites.

3.11. An estimate of the effect which this assumption has on the result can be obtained by considering the other extreme case of perfectly flexible molecules. It has been mentioned (§ 3.9) that the only effect which this has is to alter, by a multiplicative factor $z-1$, the numerical factor in one of the four terms of the grand partition function (equation (3.29)). It is easy to see that this will merely multiply the term which involves ϵ_3' in equations (3.31) and (3.32) by a factor $z-1$. Corresponding to this the value of ϵ_3 is altered, in an equally trivial manner, to give

$$\epsilon_3 = \frac{2}{3z^3(z-1)}\frac{\theta_3(z-\frac{4}{3}\theta_3)^2}{(1-\theta_1-\theta_3)^3}, \qquad (3.38')$$

and the combinatory factor for perfectly flexible molecules is

$$g(N_1, N_3, N_v) = \left[\frac{\{N_1+(3z-4)N_3/z+N_v\}!}{(N_1+3N_3+N_v)!}\right]^{\frac{1}{2}z} \frac{(N_1+3N_3+N_v)!}{N_1!\,N_3!\,N_v!}\left[\frac{z(z-1)}{\sigma}\right]^{N_3}. \qquad (3.41')$$

Thus the perfect flexibility of the trimer molecules introduces, into the combinatory factor, a factor $z-1$ for each trimer molecule.

3.12. To consider solutions of longer chain molecules by examining the detailed occupation of a central site and its z closest neighbours is excessively complicated. However, provided one is concerned with systems with zero energy of mixing it is sufficient† to examine the detailed occupation of a group of sites just large enough to accommodate one molecule of any species in the mixture. Thus provided one considers only rigid chain molecules it is sufficient to examine the detailed occupation of a collinear group of sites equal in number to the number of sub-molecules in the chain molecule. In this way Guggenheim has considered mixtures containing rigid tetramers. His analysis leads to results which are consistent with equation (3.48) below.

The free energy of mixing

3.13. The contribution to the free energy of a mixture which arises from the configurational term in the partition function is kT times the natural logarithm of the appropriate combinatory factor. Thus for a mixture of two kinds of roughly spherical molecules of about the same size the configurational contribution to the free energy of a mixture containing N_i of type i and N_j of type j is

$$-kTN_i\log\frac{N_i}{N_i+N_j}-kTN_j\log\frac{N_j}{N_i+N_j}. \tag{3.42}$$

For a mixture which contains dimer and monomer molecules the configurational contribution to the free energy is‡ from equation (3.28)

$$kT\{\tfrac{1}{2}zN_1+(z-1)N_2\}\log\frac{N_1+2(z-1)N_2/z}{N_1+2N_2}-kTN_1\log\frac{N_1}{N_1+2N_2}-$$
$$-kTN_2\log\frac{N_2}{N_1+2N_2}+kTN_2\log\frac{z}{\sigma}. \tag{3.43}$$

Expression (3.43) reduces to zero for a sample of the pure liquid of monomer molecules, when N_2 is set equal to zero. On the other hand, the pure liquid of dimer molecules has a combinatory term in its free energy, as can be seen by setting N_1 equal to zero n (3.43). This is due to the distinguishable ways in which the dimer molecules can pack amongst themselves. For the configurational term in the free energy of the pure liquid of dimers we get

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† Guggenheim, E. A., *Trans. Faraday Soc.* **41** (1945), 107.

‡ We take the case obtained by putting N_3 zero in equation (3.28).

$$kT(z-1)N_2\log\frac{z-1}{z}+kTN_2\log\frac{2z}{\sigma}. \tag{3.44}$$

The configurational term in the free energy of mixing of a mixture of dimer and monomer molecules is therefore given by ubtracting (3.44) from (3.43). This gives

$$\frac{(\Delta A)_{2,1}}{kT}=\{\tfrac{1}{2}zN_1+(z-1)N_2\}\log\frac{N_1+2(z-1)N_2/z}{N_1+2N_2}-$$
$$-N_1\log\frac{N_1}{N_1+2N_2}-N_2\log\frac{2N_2}{N_1+2N_2}+(z-1)N_2\log\frac{z}{z-1}, \tag{3.45}$$

rrespective of the value of the symmetry number σ.

The configurational term in the free energy of a mixture containing trimer and monomer molecules can be found in precisely the same way from equation (3.41) or (3.41′). Irrespective of whether the trimer molecules are flexible or inflexible, it can be shown that the free energy of mixing is given by

$$\frac{(\Delta A)_{3,1}}{kT}=\{\tfrac{1}{2}zN_1+(3z-4)N_3\}\log\frac{N_1+(3z-4)N_3/z}{N_1+3N_3}-$$
$$-N_1\log\frac{N_1}{N_1+3N_3}-N_3\log\frac{3N_3}{N_1+3N_3}+\tfrac{1}{2}(3z-4)N_3\log\frac{3z}{3z-4} \tag{3.46}$$

for all values of the symmetry number.

Mixtures containing polymer molecules

3.14. Comparison of expressions like (3.28) and (3.41) for the combinatory factor, or of (3.45) and (3.46) for the free energy of mixing, of mixtures containing dimer and trimer molecules respectively led to the construction of the combinatory factor and the free energy of mixing† for the general case in which the mixture contained polymer molecules of any number of sub-molecules. The generalization is, in fact, straightforward and merely involves writing down the simplest general formula to which those which had been evaluated for mixtures containing dimer and trimer molecules conform. Inspection of these formulae shows that the numerical factors involved are in every case the particular values of the parameters q (defined in § 2.2) for the molecule in question. Thus introducing q_2', q_3' as the values of q for chain molecules of two and three segments respectively, equations (3.45) and (3.46) can be rewritten as

$$\frac{(\Delta A)_{2,1}}{kT} = \tfrac{1}{2}z\{N_1+q_2'N_2\}\log\frac{N_1+q_2'N_2}{N_1+2N_2}-N_1\log\frac{N_1}{N_1+2N_2}-$$

$$-N_2\log\frac{N_2}{N_1+2N_2}-\tfrac{1}{2}zq_2'N_2\log q_2', \quad (3.45')$$

$$\frac{(\Delta A)_{3,1}}{kT} = \tfrac{1}{2}z\{N_1+q_3'N_3\}\log\frac{N_1+q_3'N_3}{N_1+3N_3}-N_1\log\frac{N_1}{N_1+3N_3}-$$

$$-N_3\log\frac{N_3}{N_1+3N_3}-\tfrac{1}{2}zq_3'N_3\log q_3'. \quad (3.46')$$

Once the occurrence of the values of the parameters q had been noticed, the free energy of mixing for a mixture which contained polymer molecules each consisting of r sub-molecules was given as

$$\frac{(\Delta A)_{r,1}}{kT} = \tfrac{1}{2}z\{N_1+q_r'N_r\}\log\frac{N_1+q_r'N_r}{N_1+rN_r}-N_1\log\frac{N_1}{N_1+rN_r}-$$

$$-N_r\log\frac{N_r}{N_1+rN_r}-\tfrac{1}{2}zq_r'N_r\log q_r'. \quad (3.47)$$

The corresponding formula for the combinatory factor of a mixture containing rigid, rod-like, r-mer molecules is

$$g(N_1,N_r,N_v) = \left[\frac{(N_1+q_r'N_r+N_v)!}{(N_1+rN_r+N_v)!}\right]^{\frac{1}{2}z}\frac{(N_1+rN_r+N_v)!}{N_1!\,N_r!\,N_v!}\left(\frac{z}{\sigma}\right)^{N_r}. \quad (3.48)$$

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† Miller, A. R., *Proc. Cambridge Phil. Soc.* 39 (1943), 54, § 3.

It has been seen that the perfect flexibility of trimer molecules introduces an additional factor $z-1$ per trimer molecule; for longer chains the flexibility will introduce a more complicated factor. It will in all cases introduce a factor per chain molecule which will depend on the number of sub-molecules of which the polymer is built up, the geometry of the array of sites (through the average coordination number) and the degree of flexibility enjoyed by each polymer molecule. The average contribution per polymer molecule to the combinatory factor arising, through the three factors mentioned, from the flexibility of the polymer molecules can be specified by a quantity f_r. Then, for a mixture containing r-mer molecules of any degree of flexibility, the combinatory factor can be written formally as

$$g(N_1, N_r, N_v) = \left[\frac{(N_1+q'_r N_r+N_v)!}{(N_1+rN_r+N_v)!}\right]^{\frac{1}{2}z} \frac{(N_1+rN_r+N_v)!}{N_1!\,N_r!\,N_v!}\left(\frac{zf_r}{\sigma}\right)^{N_r}. \tag{3.49}$$

3.15. In evaluating the free energy of mixing it is necessary to consider not only $g(N_1, N_r)$ but also its value when N_1 is set equal to zero, which can be denoted by $g(0, N_r)$, and to determine

$$\log\frac{g(N_1, N_r)}{g(0, N_r)}. \tag{3.50}$$

It is clear from the form of equation (3.49) that this quantity is necessarily independent of the value of f_r. Thus equation (3.47) for the free energy of mixing is valid whatever the degree of flexibility of the polymer molecules. It will be seen in the next chapter that in determining the vapour-pressure equations, and thence all the thermodynamical properties of the mixture, the only significant quantity which does not involve the ratio (3.50) is the differential coefficient $\partial \log g(N_1, N_r)/\partial N_1$; and it also must be independent of f_r. Thus the quantities with which we are concerned in determining the free energy of mixing and the vapour-pressure equations are necessarily independent of any factor which depends on the flexibility of the polymer molecules, provided only that they are as flexible in solution as in the pure species. Since the flexibility necessarily depends on the steric properties of the molecules this condition will probably be fulfilled for most solvents. Thus it is worth emphasizing that since the precise form of f_r is immaterial so far as the interesting thermodynamical quantities are concerned, it is unnecessary to evaluate it.

Thus all the quantities necessary to determine the thermodynamical properties of solutions containing polymer molecules of any number of segments have now been evaluated. Before proceeding to their evaluation we may first consider other methods which have been used to derive the combinatory factor, and secondly, present a stricter derivation of the general equation (3.49).

Direct enumeration of distinct configurations

3.16. It is clear that in principle the combinatory factor could be obtained by the direct enumeration of the distinguishable configurations of the molecules of the mixture on a quasi-crystalline array of sites. To do this it would be sufficient to consider the process by which polymer molecules are added in succession to the empty array of sites and to count the number of alternative configurations available to each successive molecule. This is a method which has been used† to allow for the differences in the size and shape of the two kinds of molecules in a mixture of dimer and monomer molecules. In this way, Fowler and Rushbrooke obtained formulae in the limiting cases of highly concentrated and extremely dilute solutions. Their formulae are asymptotically equivalent to equation (3.28) derived by Bethe's method; a fuller comparison of the results has been given elsewhere.‡ The general case of a mixture containing polymer molecules of any number of sub-molecules has been treated in a similar way by Flory§ and by Huggins,|| a brief account of whose work will now be given.

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† Fowler, R. H., and Rushbrooke, G. S., *Trans. Faraday Soc.* **33** (1937), 1272.

‡ Miller, A. R., *Proc. Cambridge Phil. Soc.* **38** (1942), 109, § 3.

§ Flory, P. J., *J. Chem. Phys.* **9** (1941), 660; ibid. **10** (1942), 51.

|| Huggins, M. L., ibid. **9** (1941), 440; *J. Phys. Chem.* **46** (1942), 151; *Ann. N.Y. Acad. Sci.* **43** (1942), 1.

3.17. Flory uses a model essentially the same as the quasi-crystalline array of sites (or of cells) which has been described in §§ 1.9, 2.1, and 2.2. He considers a mixture containing N_1 monomer and N_r r-mer molecules which can be arranged on an array containing N $(= N_1+rN_r)$ sites in all. Starting with all the sites empty, the successive addition of polymer molecules is examined. After n polymer molecules have been accommodated on the array, there are $N-nr$ sites which may be occupied by the terminal segment of the next polymer molecule to be accommodated on the array of sites. For a random mixture the average number of vacant sites which are closest neighbours to the site which is occupied by the terminal segment of the $(n+1)$th polymer molecule is $z(N-rn)/N$, and this is the number of sites available for the second segment. For the third segment, the average number of available vacant sites will be $(z-1)(N-rn)/N$, since one of the sites which are closest neighbours to that occupied by the second segment is already occupied by the terminal segment of the polymer. Flory assumes that, on the average, the number of vacant sites available for every segment beyond the third is also equal to $(z-1)(N-rn)/N$. This assumption does not allow for the fact that, for these segments (for explicitness, say, segment i), one of the closest neighbour sites of the $(i-1)$th segment may already be occupied by one of the segments $0, 1, 2,..., i-4$.

Thus this method gives too large an estimate for the number of distinguishable configurations. With this assumption, the number of configurations available to the $(n+1)$th polymer molecule is

$$\nu_{n+1} = (N-rn)^r z(z-1)^{r-2}/\sigma_r N^{r-1}, \tag{3.51}$$

where σ_r is the symmetry number of the r-mer molecules. It follows that the total number of distinguishable configurations of the molecules of the mixture is

$$\frac{1}{N_r!}\prod_{n=1}^{N_r} \nu_n, \tag{3.52}$$

where the factorial term is introduced to eliminate configurations which differ only in the interchange of two or more polymer molecules. From (3.51) and (3.52) we get for the number of configurations

$$g(N_1, N_r) = \left\{\frac{z(z-1)^{r-2}r^r}{N^{r-1}\sigma_r}\right\}^{N_r} \frac{1}{N_r!} \left\{\frac{(N/r)!}{(N/r-N_r)!}\right\}^r, \qquad (3.53)$$

so that, to this degree of approximation, the contribution of the configurational terms to the free energy is

$$-kTN_1 \log\frac{N_1}{N_1+rN_r} - kTN_r \log\frac{N_r}{N_1+rN_r} + $$
$$+kTN_r \log\{z(z-1)^{r-2}/\sigma_r\} - kT(r-1)N_r. \qquad (3.54)$$

For the pure species of r-mer molecules there is, according to Flory's method, a configurational contribution to the free energy amounting to

$$kTN_r \log\{z(z-1)^{r-2}/\sigma_r\} - kT(r-1)N_r + kTN_r \log r. \qquad (3.55)$$

Thus Flory obtains for the free energy of mixing

$$\frac{(\Delta A)_{r,1}}{kT} = -N_1 \log\frac{N_1}{N_1+rN_r} - N_r \log\frac{rN_r}{N_1+rN_r}. \qquad (3.56)$$

Introducing the volume fractions v_1 and v_r of monomer and polymer respectively, this reduces to a particularly simple form:

$$\frac{(\Delta A)_{r,1}}{kT} = -N_1 \log v_1 - N_r \log v_r. \qquad (3.57)$$

3.18. Huggins similarly computes the number of ways o arranging successive polymer molecules on a quasi-crystallin array of sites. His analysis differs from that of Flory in that h calculates approximately the effect, on the number of site available for the segments of each polymer molecule, of th blocking of sites by other, distant, segments of the same polyme molecule. By considering the average occupation of neighbouring sites by different polymer molecules and by different segments of the same polymer molecule, Huggins finds that th number of sites available to accommodate the mth $(2 < m \leqslant r$ segment of the nth polymer molecule is

$$\frac{(z-1)(1-\phi_n)}{1-2(r-1)\phi_n/rz},$$

$$\phi_n = \phi_0+(n-1)r(1-\phi_0)/N,$$

with ϕ_0 a small constant which Huggins finds to be of the order of magnitude of 0·05. He thus obtains for the number of configurations of the nth polymer molecule

$$\nu_n = \prod_{l=1}^{n} \frac{(z-1)(1-\phi_l)}{1-2(r-1)\phi_l/rz}.$$

With this value, he obtains for the free energy of mixing,

$$\begin{aligned}\frac{(\Delta A)_{r,1}}{kT} = & -N_1 \log\frac{N_1}{N_1+rN_r} - N_r \log\frac{N_r}{N_1+rN_r} + \\ & + \frac{r-1}{2r}\{z'N_1+r(z'-2)N_r\}\log\left\{1-\frac{2rN_r}{z'(N_1+rN_r)}\right\} - \\ & -\tfrac{1}{2}(r-1)(z'-2)N_r \log\frac{z'-2}{z'}, \end{aligned} \tag{3.58}$$

where z', which does not differ greatly from z, has been written for

$$z' = \frac{rz}{(r-1)(1-\phi_0)} - \frac{2\phi_0}{1-\phi_0}. \tag{3.59}$$

3.19. In the application of these formulae for the free energy of mixing to solutions of high polymers it must be remembered that the quantity r is very large, of the order of magnitude of many thousands. With this in mind, it can be seen that equations (3.47) and (3.58) are virtually identical and that equation (3.56) is the limit to which both tend as z approaches ∞. In view of what has been noted in § 3.15, it would appear that the detailed consideration of the disposition on the array of sites of each segment of each polymer molecule is unnecessary and merely introduces unwanted algebraical complications.† Another determination of the combinatory factor by calculating the number of permutations of molecules on an array of sites has been given by Münster.‡ He introduces the idea of a virtual molecule which consists of a group of monomer molecules of the same size and shape as each polymer molecule and considers the

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† A comparison of these three methods of determining the combinatory factor has been given by Gee (*Advances in Colloid Science*, 2 (1946), 145) and a general review has been given by Münster (*Koll. Zeits.*, 1948).

‡ Münster, A., *Koll. Zeits.* 105 (1943), 1; *Zeits. f. Naturfors.* 1 (1946), 311; ibid. 2 (1947), 272, 284.

number of permutations of polymer molecules and virtual molecules, allowing for the number of configurations of each molecule when one of its segments is fixed. For the free energy of dilution his result is identical with a first approximation obtained by expanding equation (3.47) as a power series in the volume fraction of the polymer.

A quite different model, applicable to a liquid near its critical point, can also be used to evaluate the entropy of mixing.† It is found that, on this model, the important parameter is the ratio of the molecular volumes, and if equation (3.47) is rewritten in terms of the volume fractions of the components, it is found to be identical with the equation which is obtained from this model of a highly imperfect gas.

It is noteworthy that determinations of the free energy of mixing on the basis of two quite different models, one of which is a good representation of a liquid near its melting-point and the other of which is a good representation of a liquid near its critical point, both lead to the same result. This increases the assurance with which equation (3.47) can be accepted. Furthermore, this result can now be deduced in a more rigorous way. To do this it is necessary to make use of some general statistical results which have been derived‡ for simple chain, branched chain, and closed ring molecules.

Basic statistical results

3.20. The physical model which is considered is the quasi-crystalline array of sites described in § 1.9, and the parameters which specify the composition of the mixture and the molecules of its constituent species have been defined in §§ 2.2 to 2.5. For the present, attention is confined to mixtures of any number of species for which the energy of mixing of each pair is zero, so that there is a random distribution of molecules on the array of sites. The total number of closest neighbour interactions in which molecules of species i are partners depends both on the number of molecules of this species and on the number of closest neighbour interactions which each molecule of this species yields. Thus the relative frequency of i—j interactions, for all values of i and j, is $q_i q_j N_i N_j$. The relative frequencies of various typical modes of occupation of a given pair of closest neighbour sites (conveniently referred to as A and B) are given in Table 2.

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† Hildebrand, J. H., *J. Chem. Phys.* **15** (1947), 225.

‡ Miller, A. R., *Proc. Cambridge Phil. Soc.* **43** (1947), 422.

TABLE 2

Relative Frequencies of Typical Modes of Occupation of a Given Pair of Sites

	Mode of occupation	*Relative frequency*
α	Both by i (excluding adjacent groups of the same i)	$q_i^2 N_i^2$
β	A by i, B by j	$q_i q_j N_i N_j$
γ	A by j, B by i	$q_i q_j N_i N_j$
δ	By adjacent groups of the same molecule i	$(r_i - q_i)N_i \sum\limits_k q_k N_k$

The definitions of X_{ii} and X_{ij} imply that the frequency of occupation of the given pair of sites in the mode α is proportional to X_{ii} and that the sum of the frequencies of occupation in the modes β and γ is proportional to X_{ij}. X_{ij} is proportional to the sum of the frequencies of occupation in the modes β and γ because these are the two possible ways in which the given pair of sites can yield an i—j pair. It therefore follows from the equations (2.3) and Table 2 that

$$\left.\begin{aligned} X_{ii} &= \frac{q_i^2 N_i^2}{2\sum\limits_k q_k N_k} \quad \text{(all } i\text{)}, \\ X_{ij} &= \frac{q_i q_j N_i N_j}{\sum\limits_k q_k N_k} \quad \text{(all } i \text{ and } j \text{ with } i \neq j\text{)}. \end{aligned}\right\} \tag{3.60}$$

It will be noticed that the last line of Table 2, referring to the mode of occupation δ, follows immediately from equations (2.5) and (3.60).

The probability that a given site, say A, is occupied by a molecule of species i is $r_i N_i / \sum\limits_k r_k N_k$. All the ways in which site A can be occupied by a molecule of species i is included in the modes of occupation indicated by α, β, and δ in Table 2. In this connexion the mode of occupation β is regarded as typical of all modes in which site A is occupied by a molecule of species i and site B is occupied by a molecule of any species other than i. Thus when we are considering all the ways in which site A can be occupied by a molecule of species i we have to consider the mode β for all values of j not equal to i. It follows therefore that the probabilities of the occupation of a given pair of sites in the various modes indicated are K times the relative frequencies given in Table 2 where the constant K is given by the equation

$$K \sum_k q_k N_k \sum_k r_k N_k = 1.$$

Without further elaboration it is therefore clear that the probabilities of occupation of a pair of sites in various typical ways for a mixture containing any number of species consisting of simple, simple chain, branched chain, or closed ring molecules are given in Table 3.

TABLE 3

Probabilities of Occupation of a Given Pair of Sites in Various Ways

	Mode of occupation	*Probability*
α	Both by i (excluding adjacent groups of the same molecule i)	$q_i^2 N_i^2 / \sum_k q_k N_k \sum_k r_k N_k$
β	A by i, B by j	$q_i q_j N_i N_j / \sum_k q_k N_k \sum_k r_k N_k$
γ	A by j, B by i	
δ	By adjacent groups of the same molecule i	$(r_i - q_i) N_i / \sum_k r_k N_k$

It will be recalled that in these formulae the parameters q_i are defined by the fact that zq_i is the number of closest neighbour interactions of a molecule of the species i, and that its value has to be determined according to the type of molecule. It should be emphasized again that these results follow from the physical meanings of the various parameters which have been introduced and do not depend upon the particular values which any of these parameters assume for any particular kind of molecule. We have already seen that for simple chain or branched chain molecules the parameters q_i have the values q'_i given by equation (2.1), while for closed ring molecules they have the values q''_i given by equation (2.2).

Statistical derivation of general formulae

3.21. The basic differential equation can be derived by a statistical argument in the following way.[†] For simplicity, the argument will be given for a binary mixture. Consider an assembly which consists of a mixture of monomer and r-mer molecules in contact with their vapour. Define two states of this assembly in the following way:

State α: N_1 monomer and N_r r-mer molecules,

state β: N_1+r monomer and N_r-1 r-mer molecules.

For a random mixture the relative frequencies of occurrence of states α and β, denoted by P_α and P_β respectively, are proportional simply to the number of distinct configurations of the given numbers of molecules of each type. Thus

$$\frac{P_\alpha}{P_\beta} = \frac{g(N_1, N_r)}{g(N_1+r, N_r-1)}, \tag{3.61}$$

an equation which merely makes use of the statistical weight. In the present case the randomness of the mixture imposes an additional constraint and the sum over all the states of the assembly reduces to the combinatory factor which is the degeneracy of the state which has the given (constant) value of the configurational energy.

If the total number of sites is kept fixed and N_r is decreased by unity so that N_1 is necessarily increased by r, then the increment in $\log g(N_1, N_r)$ is given by

$$\begin{aligned}[\Delta \log g(N_1, N_r)]_{\substack{\Delta N_r=-1\\ \Delta N_1=r}} &= \log g(N_1+r, N_r-1) - \log g(N_1, N_r)\\ &= -\log\frac{g(N_1, N_r)}{g(N_1+r, N_r-1)}.\end{aligned}$$

Thus, using equation (3.61), this yields

$$\left[\frac{\partial \log g(N_1, N_r)}{\partial N_r}\right]_N + \log\frac{P_\alpha}{P_\beta} = 0. \tag{3.62}$$

Now consider the occupation of all but a selected group (Γ) of sites, r in number, which are interrelated in such a way that they can accommodate an r-mer molecule. Let N_1 monomer molecules and N_r-1 r-mer molecules be arranged in any configuration, specified by C_r, on the remaining $N-r$ sites: denote the probability of the particular configuration C_r by P_r. The occupation of Γ by an r-mer molecule is directly proportional to N_r. Then, since there is complete randomness in the occupation of the sites, the relative frequency of the configuration in which an r-mer molecule occupies Γ and the remaining $N-r$ sites are occupied in the manner C_r is

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[†] Miller, A. R., unpublished results.

$$P_r N_r/N, \tag{3.63}$$

apart from a factor which may depend on r, q, z, and T but is independent of N_1 and N_r. This is the frequency of occurrence of a state in which there are N_1 monomer and N_r r-mer molecules in the complete assembly, that is, the state α. The probability of the occupation of Γ by r monomer molecules is, by an extension of the result given in lines β and γ of Table 3,

$$\frac{N_1}{N}\left(\frac{N_1}{N_1+qN_r}\right)^{r-1}. \tag{3.64}$$

Thus the probability of the configuration in which monomer molecules occupy Γ and the remaining sites are occupied in the manner C_r is

$$P_r\frac{N_1}{N}\left(\frac{N_1}{N_1+qN_r}\right)^{r-1}. \tag{3.65}$$

This is the probability of a state in which there are N_1+r monomer molecules and N_r-1 r-mer molecules, that is, the state β. Thus the ratio of P_α to P_β can be obtained from equations (3.63) and (3.65); the result is independent of P_r, that is, it is independent of the configuration of molecules on the sites outside Γ, and so must be valid whatever that configuration. Thus

$$\rho\frac{P_\alpha}{P_\beta}=\frac{N_r}{N_1}\left(\frac{N_1+qN_r}{N_1}\right)^{r-1}, \tag{3.66}$$

where ρ may depend on r, q, z, and T but is independent of N_1 and N_r. Substitution of the value of P_α/P_β given by equation (3.66) in equation (3.62) yields the differential equation

$$\left[\frac{\partial\log g(N_1,N_r)}{\partial N_r}\right]_N=\log\rho+r\log(N-rN_r)-\log N_r-$$
$$-(r-1)\log\{N-(r-q)N_r\}, \tag{3.67}$$

where N_1 has been replaced by its value in terms of N and N_r which are taken as the variables. In integrating equation (3.67) the constant of integration is determined by the condition that when N_r is zero, $g(N_1, N_r)$ must reduce to unity. Integration of equation (3.67) yields, for the combinatory factor, the expression

$$\log g(N_1, N_r) = -\log N_1! - \log N_r! + \frac{r-1}{r-q}\log(N_1+qN_r)! - \\ -\frac{q-1}{r-q}\log(N_1+rN_r)! + N_r \log \rho. \tag{3.68}$$

In this formula the parameters q have to be given the values q' or q'', defined by equations (2.1) and (2.2), which are appropriate to simple and branched chain and to closed ring molecules respectively. For simple chain and branched chain molecules

$$z(r-q) = 2(r-1),$$

so that

$$\frac{r-1}{r-q} = \tfrac{1}{2}z, \quad \frac{q-1}{r-q} = \tfrac{1}{2}z-1. \tag{3.69}$$

If the values of the coefficients of the terms in equation (3.68) are replaced by these values, then it is easily seen that equation (3.68) is identical with equation (3.49) with N_r put equal to zero. Thus the derivation of equation (3.68) by the statistical method of this section leads to the same result as the mathematical extrapolation by which equation (3.54) was first constructed.†

3.22. The physical significance of ρ can be determined‡ by considering the case in which $N_1 \gg rN_r$. In this case $(r-q)N_r$ can be neglected compared with N and equation (3.68) becomes asymptotically equivalent to

$$g(N_1, N_r) \sim \frac{(N_1+rN_r)^{N_r}}{N_r!}\rho^{N_r} \quad (N_1 \gg rN_r). \tag{3.70}$$

Provided $N_1 \gg rN_r$ the factor which multiplies ρ^{N_r} in the right-hand member of equation (3.70) is the number of ways of choosing N_r out of N sites. It may therefore be interpreted as the number of ways of choosing sites for one selected element in each of the N_r r-mer molecules. Consequently the parameter ρ

must denote the number of distinct configurations of a polymer molecule when one of its elements is fixed on a given site. This verifies that ρ is a configurational factor which depends only on the geometry of the molecules and of the array of sites. It is also related to the factor f_r which was introduced in § 3.14 to allow for the contribution per polymer molecule to the combinatory factor due to the flexibility of the polymer molecules. The relation between ρ and f_r is given by

$$\sigma_r \rho = z f_r. \tag{3.71}$$

Although it is not necessary to evaluate ρ or f_r in order to determine the thermodynamical properties of the mixture,[†] it is of interest to note the values assumed by ρ for a number of simple cases in which its value can be deduced from a knowledge of its physical significance. In the trivial case of a monomer molecule ρ is unity. For a dimer molecule ρ is z/σ, where σ is the symmetry number of the molecule. Substituting this value of ρ and $r = 2$ in equation (3.68) one recovers equation[‡] (3.28). In the case of trimer molecules three cases have to be considered. If the molecules are linear and rigid ρ is z/σ; if they are linear and flexible ρ is $z(z-1)/\sigma$. Substituting these values and $r = 3$ in equation (3.68) one recovers equations[§] (3.41) and (3.41′). If the trimer molecules are non-linear and rigid, then ρ is zz'/σ, where z' is the number of alternative sites for the third segment when the first two segments of the trimer molecule have been placed. For molecules which occupy more than three sites there are several alternatives. The minimum value of ρ, which occurs for linear rigid molecules, is z/σ. An upper bound to possible values of ρ is $z(z-1)^{r-2}/\sigma$. This value must be slightly greater than the precise value of ρ for flexible molecules because it includes certain configurations in which the chain molecule bends back on itself and two segments occupy the same site; such configurations should be excluded, but the error due to their inclusion is probably small.

[†] Miller, A. R., *Proc. Cambridge Phil. Soc.* **39** (1943), 62–3; Guggenheim, E. A., *Proc. Roy. Soc.* A **183** (1944), 208–10; cf. § 3.15 above.

[‡] Chang, T. S., *Proc. Cambridge Phil. Soc.* **35** (1939), 265, equation (33); Miller, A. R., ibid. **38** (1942), 109, equation (4).

[§] Miller, A. R., ibid. **38** (1942), 109, equations (33) and (39).

Kinetic derivation of combinatory formulae

3.23. The general formula given in equation (3.68) can also be derived by kinetic arguments using the principle of detailed balancing.† Correct equilibrium conditions can be determined by considering an arbitrary elementary process and its inverse, since in equilibrium any single process balances its inverse process. For the present application of the principle of detailed balancing the elementary processes chosen for consideration are (i) the evaporation of an r-mer molecule from a selected group of r sites and the simultaneous condensation on these sites of r monomer molecules from the gas phase, and its inverse process (ii) which consists of the evaporation of r monomer molecules from the same group of r sites and the simultaneous condensation on them of an r-mer molecule from the gas phase. The rate at which the first process takes place depends directly on the rth power of p_1, the partial pressure of the monomer molecules in the gas phase, and the frequency of occupation of the group of sites Γ by an r-mer molecule. It is therefore directly proportional to

$$p_1^r \frac{N_r}{N_1+rN_r}. \tag{3.72}$$

The rate at which the second process takes place depends directly on the partial pressure p_r of the r-mer molecules in the gas phase and on the frequency of occupation of Γ by r monomer molecules. Using equation (3.64) it is therefore directly proportional to

$$p_r \frac{N_1}{N_1+rN_r}\left(\frac{N_1}{N_1+qN_r}\right)^{r-1}. \tag{3.73}$$

In equilibrium these two rates must be equal, whence

$$C\frac{p_r}{p_1^r} = \frac{N_r}{N_1}\left(\frac{N_1+qN_r}{N_1}\right)^{r-1}, \tag{3.74}$$

where C depends on r, q, and z and on the temperature T but is independent of N_1 and N_r.

The relation between the partial pressure p of a perfect gas and its absolute activity λ is

$$p = \lambda kTf(T),$$

† Guggenheim, E. A., *Proc. Roy. Soc.* A **183** (1944), 203.

where $f(T)$ is the partition function of a molecule in the gas phase apart from the volume factor. Since λ/p is a function of T only, equation (3.74) can be replaced by

$$\rho\frac{\lambda_r\phi_r}{(\lambda_1\phi_1)^r} = \frac{N_r}{N_1}\left(\frac{N_1+qN_r}{N_1}\right)^{r-1}, \tag{3.75}$$

where ρ, which can depend only on r, q, and z, is independent of T and of N_1 and N_r; and ϕ_1 and ϕ_2 respectively are used to denote the partition functions of monomer and r-mer molecules attached to specified sites.

The Gibbs function is related to the absolute activities by the equation

$$dG = \mu_1\,dN_1+\mu_r\,dN_r = kT\log\lambda_1\,dN_1+kT\log\lambda_r\,dN_r. \tag{3.76}$$

Thus, taking N and N_r as the variables,

$$\left(\frac{\partial G}{\partial N_r}\right)_N = kT\log\frac{\lambda_r}{\lambda_1^r}. \tag{3.77}$$

The combinatory factor is related to the thermodynamical functions by the equation

$$-\frac{A}{kT} = -\frac{G}{kT} = \log g(N_1, N_r)+N_1\log\phi_1+N_r\log\phi_r, \tag{3.78}$$

assuming the pressure to be small. Equations (3.75), (3.77), and (3.78) yield the differential equation (3.67) and the result already given in equation (3.68).

3.24. Since the methods which have been used in §§ 3.21 and 3.23 are concerned with systems with zero energies of mixing, the assumption of complete randomness of mixing is valid and does not introduce any error. There is, however, a concealed error in the interpretation of complete randomness in the neighbourhood of a site occupied in a specified way, and this implies that equation (3.64) is not exact. This concealed error is due to the fact that segments from different chain molecules may be competing for the same neighbouring site. It is, however, likely to be small. The assumption of complete randomness, though probably a good approximation for simple chain molecules, is not quite so good for branched chain molecules, and is least satisfactory for closed ring molecules. It will appear below that applied to simple chain molecules it involves the same sort of approximation as arises in the extrapolation (§ 3.14) by which the results for mixtures containing dimer and trimer molecules have been generalized to cover the case of mixtures containing polymer molecules.

3.25. The methods which have been described in §§ 3.21 and 3.23 can be extended immediately to examine systems which consist of any number of species containing any types of molecules. In fact, from the form of equation (3.68) and the independence, for simple chain and branched chain molecules, of the coefficients of the terms in this equation from r and q, the extension is obvious.† We obtain

$$\log g(N_i) = \tfrac{1}{2}z\log\Big(\sum_i q_i N_i\Big)! - \sum_i \log N_i! - (\tfrac{1}{2}z-1)\log\Big(\sum_i r_i N_i\Big)! + \\ + \sum_i N_i \log \rho_i. \quad (3.79)$$

For closed ring molecules, on the other hand,

$$z(r-q) = 2r,$$

so that

$$\frac{r-1}{r-q} = \frac{1}{2}\frac{r-1}{r}z, \qquad \frac{q-1}{r-q} = \frac{1}{2}\frac{r-1}{r}z-1,$$

and in this case the coefficients of the terms in equation (3.68) are not independent of r and q. However, in all applications to high polymers, $r \gg 1$ so that $(r-1)/r$ differs only insignificantly from unity; neglecting the difference between $(r-1)/r$ and unity cannot cause as great an error as is inherent in the interpretation of complete randomness. Thus to the approximation inherent in the derivation of equation (3.68), equation (3.79) is valid also if some of the species consist of closed ring molecules. This general formula can be derived by a simple extension of the argument of either §§ 3.21 or 3.23, and such a mathematical treatment confirms that equation (3.79) is directly applicable to systems of any number of species which consist of simple chain or branched chain molecules, and, provided r is so great that $(r-1)/r$ differs negligibly from unity, it is applicable also when some of the species consist of closed ring molecules. As we shall be concerned to apply these formulae only to binary monomer-polymer systems, the mathematical details for the general case[†] of many components will not be given here. It should be noted, however, that with our interpretation of complete randomness[‡] equations (3.54) and (3.68) for a monomer-polymer system apply in all cases with the appropriate values of the parameters r and q.

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† Guggenheim, E. A., *Proc. Roy. Soc.* A **183** (1944), 203, § 8.

[†] Miller, A. R., unpublished results.

[‡] See § 3.24 above.

IV

COMPARISON OF THEORY WITH EXPERIMENT

4.1. We have seen (§ 1.14) that the partial potentials in the mixture (liquid phase) are related to those of the corresponding pure liquids by equations of the form

$$\mu_i^l = \mu_{i,0}^l + \left(\frac{\partial \Delta G}{\partial N_i}\right)_{T,p} \quad \text{(all } i\text{)}, \tag{1.24}$$

where ΔG is the Gibbs free energy of mixing, which is defined by the equation

$$G = \sum_i G_i + \Delta G,$$

where the G_i are the free energies of the respective species and G is that of the mixture. The partial molar free energy of mixing of the mixture by the species i is defined by

$$\Delta G_i = L\left(\frac{\partial \Delta G}{\partial N_i}\right)_{T,p}, \tag{4.1}$$

where L is Avogadro's number.

We have also seen that the partial potentials in the vapour phase for the solution and the pure species are related by equations

$$\mu_i^v = \mu_{i,0}^v + kT \log \frac{p_i}{p_{i,0}} \quad \text{(all } i\text{)} \tag{1.28}$$

provided the vapour behaves as a perfect gas. For equilibrium it is necessary that the partial potentials in the liquid and vapour phases should be equal. Thus the preceding equations yield

$$\Delta G_i = L\left(\frac{\partial \Delta G}{\partial N_i}\right)_{T,p} = RT \log \frac{p_i}{p_{i,0}} \quad \text{(all } i\text{)}. \tag{4.2}$$

It follows that the free energy of dilution can be calculated from experimental measurements of vapour pressure or of any other property which is related to it thermodynamically. Such quantities are the osmotic and swelling pressures and the depression of the freezing-point. Measurements of all of these have been made in studying solutions of high polymers and gels. Vapour and osmotic pressure measurements have proved most tractable.

4.2. Many determinations have been made of the vapour pressure of solutions of high polymers. The quantities to be measured experimentally are the vapour pressure and the concentration of the solution. The latter can be measured either by analysis of the solution or by transferring a measured amount of liquid from a reservoir on to the polymer. The former was the method adopted by Stamberger,[†] who first pointed out clearly the precautions which are essential in making vapour-pressure determinations on such systems. The second method is more convenient experimentally and makes it possible to use a simpler type of apparatus.[‡]

Osmotic-pressure measurements on solutions can be extended to very high dilution. In this way measurements are obtained in a region of the concentration range not otherwise accessible. In making measurements of the osmotic pressure[§] both static and dynamic methods have been used. In the former methods, time is allowed for osmotic equilibrium to be attained and the osmotic pressure is measured by the difference in hydrostatic pressure between cells containing the solution and the pure solvent. In the latter methods, the rate of osmosis is measured as a function of an applied hydrostatic pressure and the osmotic pressure is determined as the hydrostatic pressure at which osmosis just ceases.

Swelling pressure does not differ thermodynamically from osmotic pressure but may be distinguished by the fact that the high polymer is not dispersed, so that the experimental techniques are different. It provides a possible means of carrying out experiments in the region of small vapour-pressure lowering and has been used to obtain measurements on rubber.[||]

The depression of the freezing-point of low molecular polymers has also been measured,[†] but for dilute solutions of rubber in benzene the freezing-point does not differ perceptibly from that of pure benzene. Measurements of the freezing-point of rubber in camphor have been attempted,[‡] but it has been shown[§] that unless the experiments are carried out *in vacuo* the rubber undergoes severe degradation and that when the measurements are made *in vacuo* on solutions sufficiently dilute to be fluid the freezing-point of the solution is indistinguishable from that of pure camphor.

[†] Stamberger, P., *J. Chem. Soc.* (1929), 2318.

[‡] Gee, G., and Treloar, L. R. G., *Trans. Faraday Soc.* **38** (1942), 147.

[§] Schulz, G. V., *Z. physikal. Chem.* A **176** (1936), 317; Carter, S. R., and Record, B. R., *J. Chem. Soc.* (1939), 660; Gee, G., *Trans. Faraday Soc.* **36** (1940), 1162; Meyer, K. H., and Boissonnas, C. G., *Helv. Chim. Acta*, **23** (1940), 430; Flory, P. J., *J. Amer. Chem. Soc.* **65** (1943), 375; Fuoss, R. M., and Mead, D. J., *J. Phys. Chem.* **47** (1943), 59.

[||] Posniak, G., *Koll.-Beihefte*, **3** (1912), 417.

From this brief outline it appears that vapour-pressure measurements and osmotic-pressure determinations have provided the most useful data in the study of the thermodynamical properties of solutions of high polymers. Details of the apparatus and of the methods used can be found in a review by Gee.[‖] We now consider some typical results and compare them with the theory which has been developed in Chapter III.

Vapour-pressure equations

4.3. For a mixture with zero energy of mixing and containing N_i monomer and N_r r-mer molecules the partition function is

$$g(N_1, N_r)\phi_1^{N_1}\phi_r^{N_r},$$

where $g(N_1, N_r)$ is the combinatory factor determined by equation (3.64) with N_v set equal to zero and ϕ_1, ϕ_r are the partition functions, apart from the configurational factors, of monomer and r-mer molecules respectively. Assuming the pressure to be small, the Helmholtz and Gibbs free energies of the mixture are given by

$$-\frac{A}{kT} = -\frac{G}{kT} = \log g(N_1, N_r)+N_1\log\phi_1+N_r\log\phi_r. \quad (4.3)$$

[†] Kemp, A. R., and Peters, R. H., *Ind. Eng. Chem.* 33 (1941), 1263; ibid. 34 (1942), 1192.

[‡] Pummerer, R. et al, *Ber.* 60 (1927), 2167; ibid. 62 (1929), 2628; *Kautschuk* 5 (1929), 129.

[§] Gee, G., *Trans. Faraday Soc.* 38 (1942), 109.

[‖] Gee, G., *Advances in Colloid Science*, 2 (1946), 145.

The free energy of mixing is therefore given by

$$\frac{\Delta G}{kT} = \log g(0, N_r) + \log g(N_1, 0) - \log g(N_1, N_r)$$

$$= \log N_1! - \tfrac{1}{2}z \log \frac{(N_1+qN_r)!}{(qN_r)!} + (\tfrac{1}{2}z-1)\log \frac{(N_1+rN_r)!}{(rN_r)!}. \quad (4.4)$$

It therefore follows, by differentiating equation (4.4) with respect to N_1 and N_r, that the molar free energy of dilution of the solution by the solvent is

$$\frac{\Delta G_1}{RT} = \log N_1 - \tfrac{1}{2}z \log(N_1+qN_r) + (\tfrac{1}{2}z-1)\log(N_1+rN_r), \quad (4.5)$$

and that the molar free energy of concentration of the solution by the solute is

$$\frac{\Delta G_r}{RT} = (\tfrac{1}{2}z-1)r \log \frac{N_1+rN_r}{N_r} - \tfrac{1}{2}zq \log \frac{N_1+qN_r}{N_r}. \quad (4.6)$$

It has been seen, equation (4.2) above, that, for each species i, the vapour-pressure equations are given by

$$\Delta G_i = RT \log \frac{p_i}{p_{i,0}}. \quad (4.2)$$

Using the values of the partial molar free energies of mixing given by equations (4.5) and (4.6) in equation (4.2), we obtain the vapour-pressure equations

$$\frac{p_1}{p_{1,0}} = \frac{N_1(N_1+rN_r)^{\frac{1}{2}z-1}}{(N_1+qN_r)^{\frac{1}{2}z}}, \quad (4.7)$$

$$\frac{p_r}{p_{r,0}} = \frac{N_r(N_1+rN_r)^{(\frac{1}{2}z-1)r}}{(N_1+qN_r)^{\frac{1}{2}zq}} \quad (4.8)$$

in terms of the mole fractions of the components.† The departure of the vapour pressure given by these equations from Raoult's law is illustrated by the curves plotted in Fig. 2, in which the relative vapour pressures of both solute and solvent are plotted as functions of the molar fraction of the solute for

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† Miller, A. R., *Proc. Cambridge Phil. Soc.* 39 (1943), 54, equations (29) and (30); Guggenheim, E. A., *Proc. Roy. Soc.* A 183 (1944), 203, equations (6.1), (6.2), (6.5), and (6.6).

various values of r, the number of segments in the polymer. In this diagram the full lines give the relative vapour pressure of the solvent and the broken lines that of the solute. For each component of the solution the straight lines give the vapour pressure for a mixture which obeys Raoult's law. The curves showing departures from this law are, in order of increasing curvature, for mixtures of monomers with dimers, trimers, and polymers containing ten segments. These curves show the influence of size effects on the vapour-pressure equations, and they indicate that for a value of r as small as 10 there is already a considerable departure from the laws of ideal solutions even when the energy of mixing is zero.

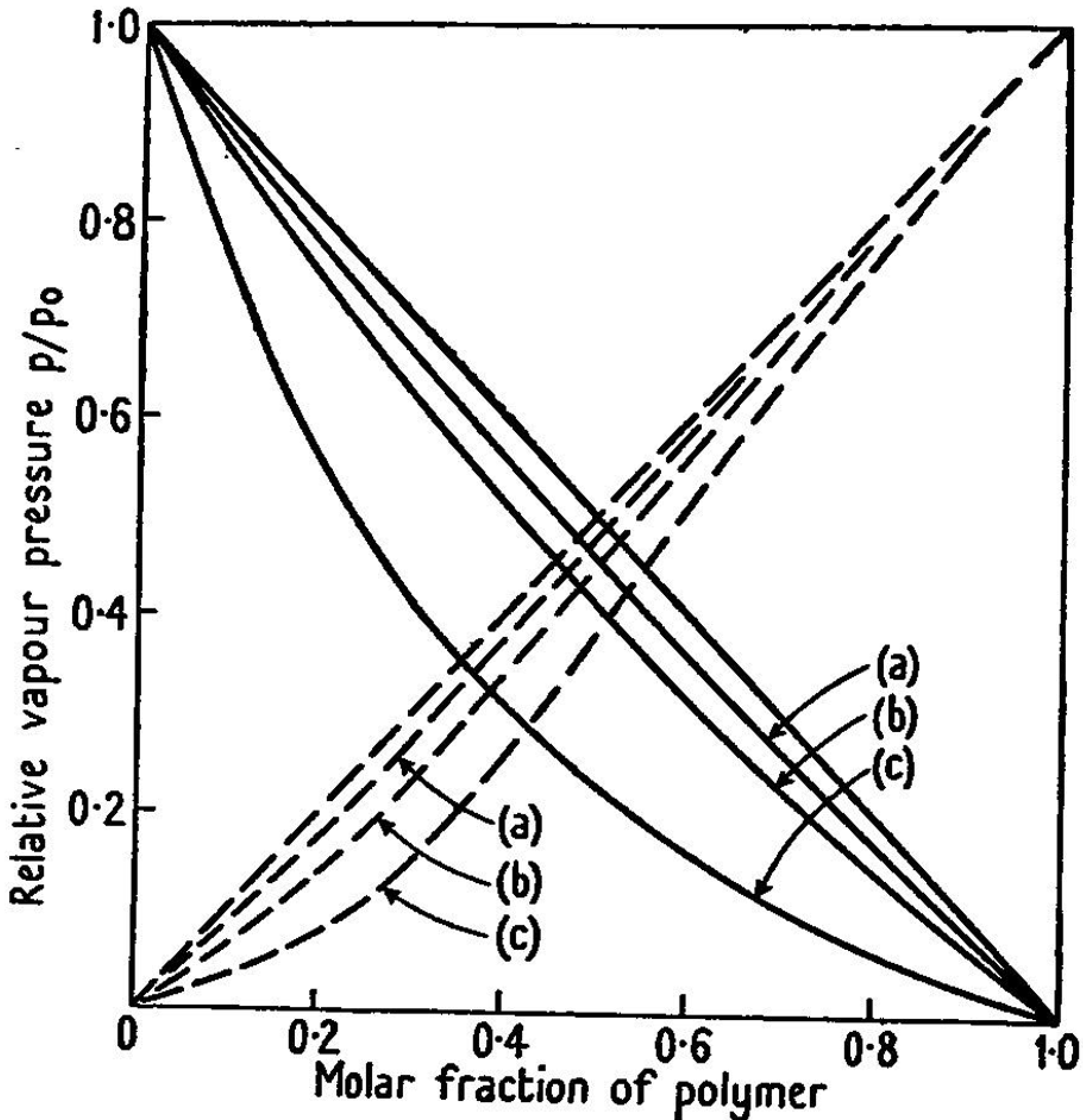

FIG. 2. The effect of differences in the sizes of the constituent molecules on the vapour-pressure equations of solutions. The full lines give the relative vapour pressures for the solvent and the broken lines for the solute. In each case curves (*a*) are for a mixture of dimers and monomers, curves (*b*) for a mixture of trimers and monomers, curves (*c*) for a mixture of polymers of ten segments with monomers. The straight lines are for a mixture which obeys Raoult's law.

Let us introduce v_r to specify the volume fraction of the polymer (r-mer molecules), so that $1-v_r$ is the volume fraction of the monomer. Then

$$v_r = \frac{rN_r}{N_1+rN_r},$$

and, since, for simple or branched chain molecules

$$(\tfrac{1}{2}z-1)r = \tfrac{1}{2}zq-1,$$

equations (4.7) and (4.8) can be written in the form

$$\frac{p_1}{p_{1,0}} = \frac{1-v_r}{\{1-(r-q)v_r/r\}^{\frac{1}{2}z}}, \tag{4.9}$$

$$\frac{p_r}{p_{r,0}} = \frac{v_r}{\{1-(r-q)v_r/r\}^{\frac{1}{2}zq}}, \tag{4.10}$$

which is appropriate to simple or branched chain molecules.

The osmotic pressure can be immediately deduced. It is related to the partial vapour pressure of the solvent in solution and the vapour pressure of the pure solvent by an equation which can be written

$$\int\limits_0^\pi v_1\,d\pi = RT\log\{p_{1,0}/p_1\},$$

where v_1 is the partial molar volume of the solvent (monomer), π is the osmotic pressure, and the other symbols have the meanings already specified in earlier sections of this chapter. It has been shown† that over the entire range of concentration the volume of mixing for mixtures of rubber and benzene is accurately zero. It follows that the partial molar volume of benzene in such mixtures is equal to the molar volume of pure liquid benzene. We therefore assume that v_1 is independent of the concentration and has the constant value $v_{1,0}$, the molar volume of the pure solvent. This gives

$$\pi = \frac{RT}{v_{1,0}}\log\frac{p_{1,0}}{p_1} \tag{4.11}$$

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† Posnjak, G., *Koll.-Beihefte*, 3 (1912), 417, showed that for rubber-benzene mixtures in which the volume fraction of benzene varied from 0·34 to 0·98, the sum of the separate volumes was within 1 per cent. of the volume of the mixture. Similar results have been obtained by Gee, G., and Treloar, L. R. G., *Trans. Faraday Soc.* 38 (1942), 147, in the range 0·012 to 0·332 of the weight fraction of benzene. For rubber-benzene mixtures the volume and weight fractions are almost identical, so that these measurements cover the whole range of concentrations.

for the osmotic pressure. For dilute solutions this reduces to the well-known formula

$$\pi = \frac{RT}{v_{1,0}}\frac{\Delta p_1}{p_{1,0}},$$

where Δp_1 is the vapour-pressure lowering.

From equations (4.9) and (4.11) the osmotic pressure of a solution of a high polymer is given by

$$\pi = \tfrac{1}{2}z\frac{RT}{v_{1,0}}\log\frac{N_1+qN_r}{N_1+rN_r}-\frac{RT}{v_{1,0}}\log\frac{N_1}{N_1+rN_r}. \tag{4.12}$$

In the region of osmotic interest, $rN_r \ll N_1$. Expanding the logarithm in equation (4.12) and neglecting terms containing higher than the second power of $rN_r/(N_1+rN_r)$, yields

$$\pi = \frac{RT}{v_{1,0}}\left\{\frac{N_r}{N_1+rN_r}+\left(\frac{1}{2}-\frac{1}{z}\right)\left(1-\frac{1}{r}\right)^2\left(\frac{rN_r}{N_1+rN_r}\right)^2\right\}. \tag{4.13}$$

In terms of the volume fraction of the polymer in the solution this can be written

$$\pi = RT\left\{\frac{v_r}{V_r}+\left(\frac{1}{2}-\frac{1}{z}\right)\frac{v_r^2}{v_{1,0}}\right\}, \tag{4.14}$$

where $V_r = rv_{1,0}$ and is the partial molar volume of the polymer in solution. If c gm.cm.$^{-3}$ is the concentration of the solution and ρ_r, M_r are the density and the molecular weight of the polymer, this equation may be written in the form

$$\frac{\pi}{c} = \frac{RT}{M_r}+\left(\frac{1}{2}-\frac{1}{z}\right)\frac{RT}{\rho_r^2 v_{1,0}}c. \tag{4.15}$$

Measurements on polystyrene

4.4. Measurements of the vapour pressure of solutions of polystyrene in various solvents have been carried out[†] and the results for non-polar solvents can be compared immediately with the vapour-pressure equation given above[‡] as equation (4.9). The experimental points which were obtained for solutions of polystyrene in toluene and in benzene are plotted in Figs. 3 and 4. Both sets of measurements were carried out at 20° C., hose with benzene as solvent using polystyrene of molecular veight 500,000 and those with toluene as solvent using poly-tyrene of molecular weight 200,000; the molecular weight was stimated from viscosity measurements at various concentra-ions. The full line drawn in each figure is calculated from

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[†] Baughan, E. C., *Trans. Faraday Soc.*, **44** (1948), 495.

[‡] I am indebted to Professor Baughan for details of his experimental results before publication.

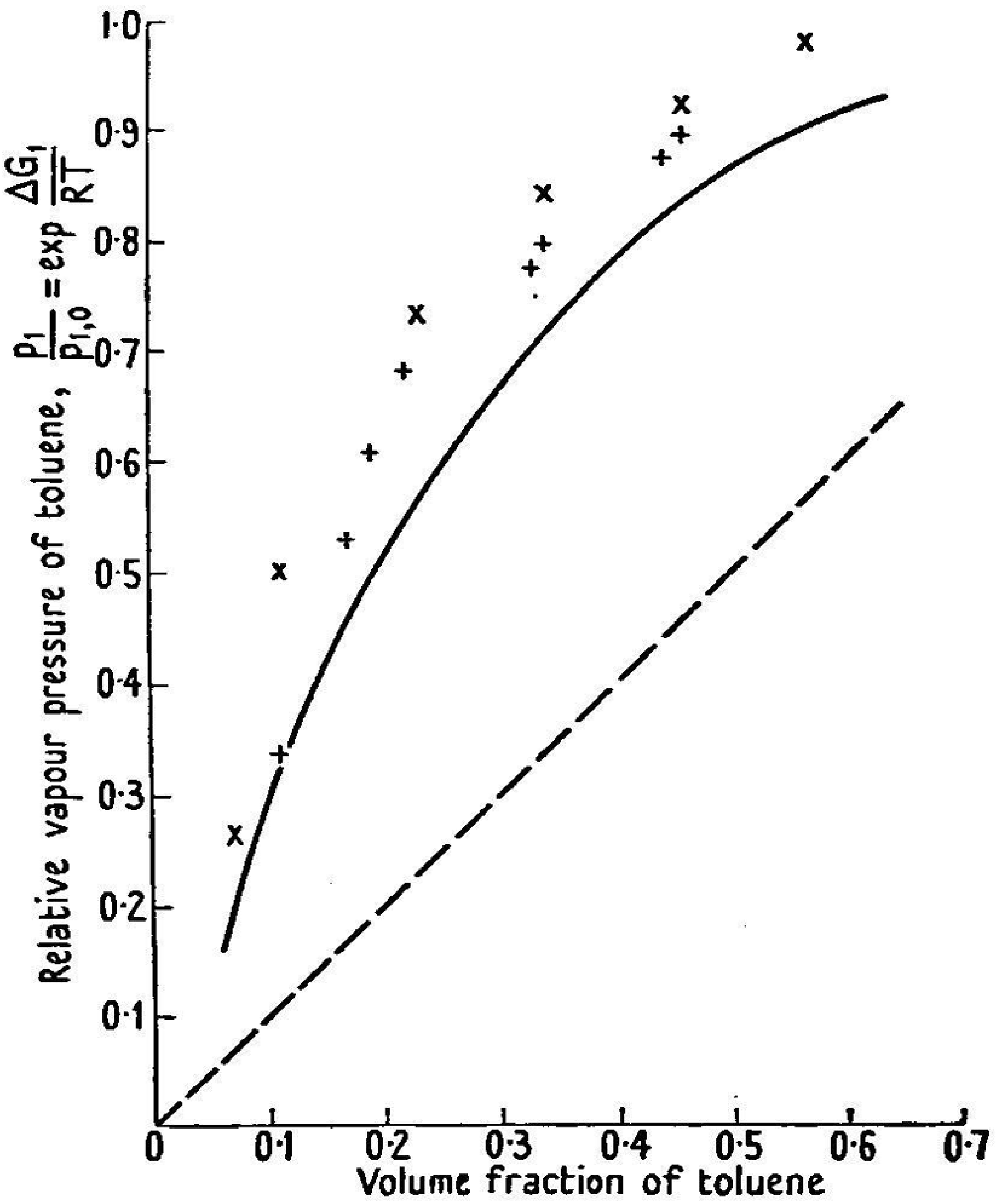

FIG. 3. Variation of the vapour pressure of a polystyrene-toluene mixture. × experimental points, vapour pressure increasing; + experimental points, vapour pressure decreasing (after Baughan); ——— theoretical curve (for $z = 6$); - - - - system obeying Raoult's law.

equation (4.9), and so shows the effect of different sizes and shapes of the molecules according to the theory developed in Chapter III without allowing for the interactions between the molecules. The dotted straight line is the relation between the vapour pressure of the solvent and the volume fraction for a system which obeys Raoult's law. The significance of these results will be discussed in § 4.6 below after similar results for rubber-benzene systems have been presented.

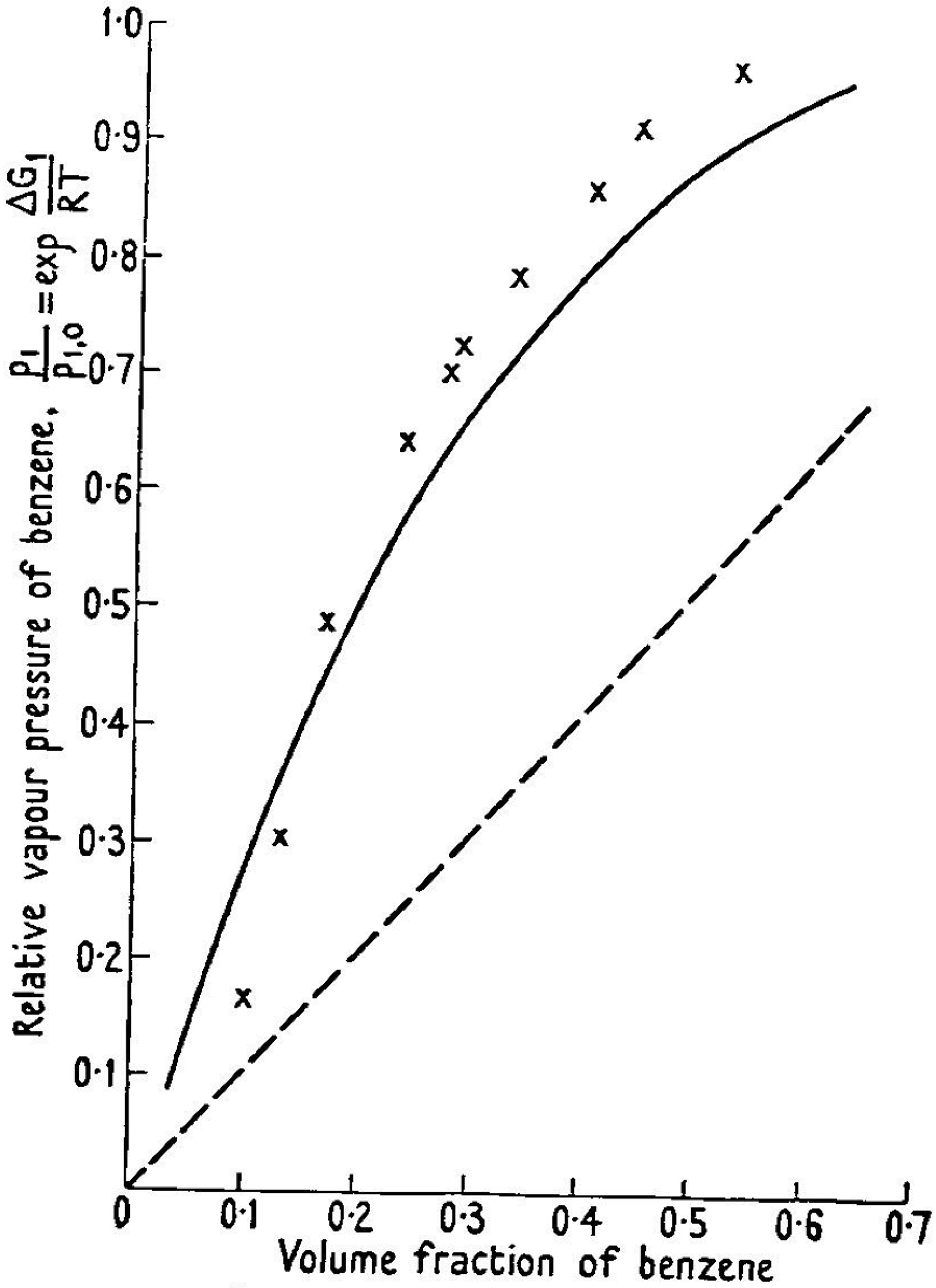

FIG. 4. Variation of the vapour pressure of a polystyrene-benzene mixture; × experimental points (after Baughan); ——— theoretical curve (for $z = 6$); – – – – system obeying Raoult's law.

Measurements on rubber

4.5. Similar results have been found for vapour-pressure measurements on rubber-benzene systems.†

With volume fractions of benzene less than 0.015 a Macleod gauge was used to measure the relative vapour pressures. For volume fractions of benzene up to 0·8, a region which had been covered in earlier measurements,‡ the relative vapour pressures f the solution and pure benzene were measured by a direct nanometric method. For solutions with volume fractions of enzene exceeding 0·8 the direct manometric method was napplicable and values were obtained by allowing a rubber olution to come into equilibrium with a solution of triolein in

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† Gee, G., and Treloar, L. R. G., *Trans. Faraday Soc.* 38 (1942), 147.

‡ Stamberger, P., *J. Chem. Soc.* (1929), 2318; Lens, J., *Rec. Trav. Chim.* 51 (1932), 971.

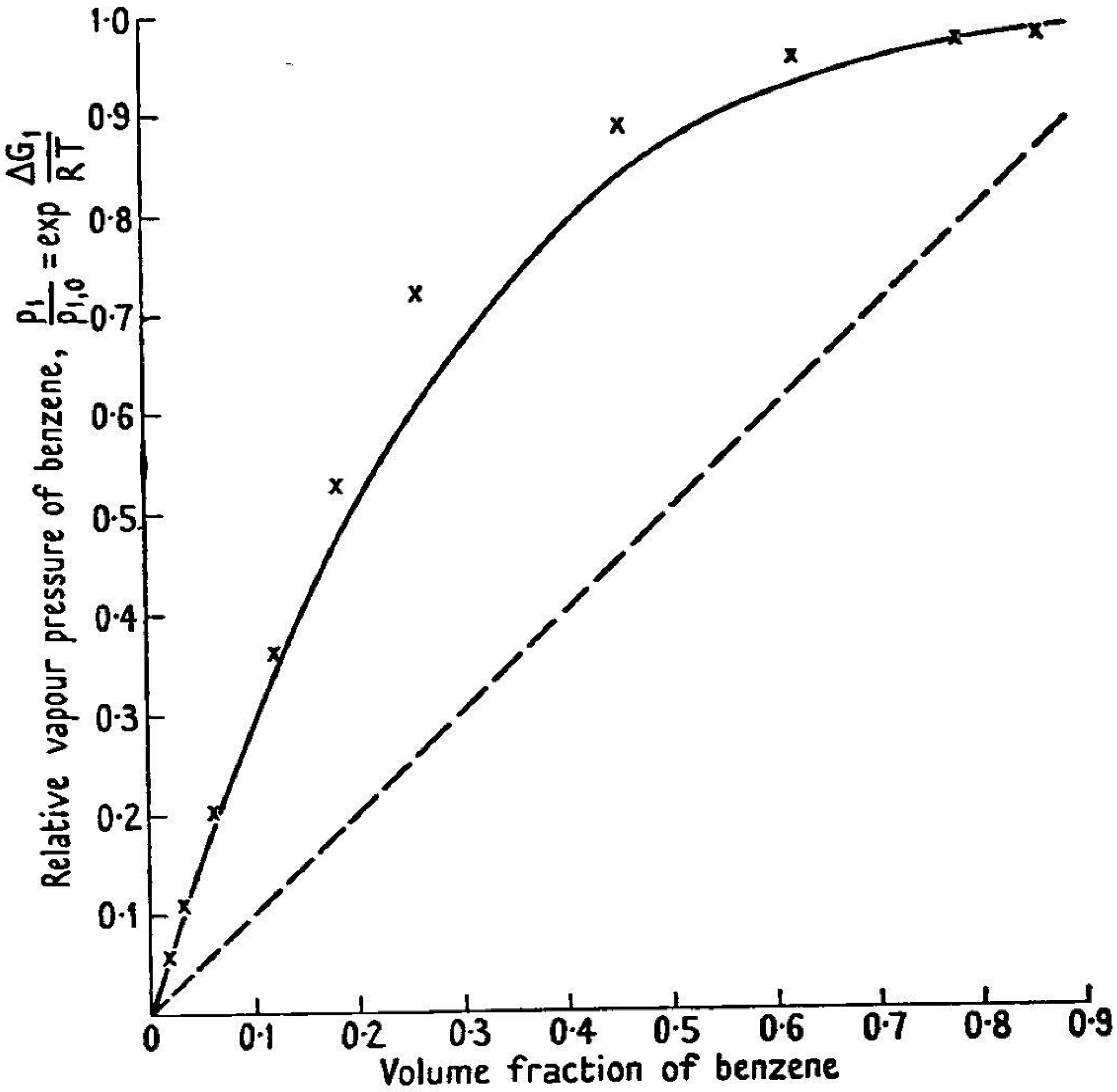

Fig. 5. Variation of the vapour pressure of the rubber-benzene system; × experimental points; ——— theoretical curve (for $z = 6$); – – – – system obeying Raoult's law.

benzene of known concentration. In the equilibrium state the vapour pressures of the two solutions are equal, so that the relative vapour pressure of the rubber-benzene system could be calculated from that of the triolein. These measurements extended over the range 0·65 to 0·95 of volume fractions of benzene. The rest of the concentration range was covered by osmotic-pressure measurements. The results of all these measurements are shown plotted in Fig. 5. Again the full line shows the vapour-pressure curve calculated from equation (4.9) and the dotted curve is that corresponding to Raoult's law.

Discussion of vapour-pressure curves

4.6. These diagrams exhibit two features of note. The first is the wide divergence of the experimental results from Raoult's law. The second is that the curve calculated from equation (4.9) is in fair agreement with the experimental results, so that the greater part of the divergence from the laws of ideal solutions is accounted for by the theory which has been given in the preceding chapter. It therefore appears that the differences in the sizes and shapes of the molecules of the constituent species of the mixture play a predominant part in producing divergence from the behaviour of ideal solutions. Other sources of departure from the laws of ideal solutions will be considered in the closing chapter of this monograph, but it is clear that, although there may be some regions of concentration in which they assume a greater importance, the effects due to them must rather appear as refinements to the theory which has been developed so far. It should, however, be noted that the measurements on polystyrene do not extend to the region of extreme dilution and that although the measurements on the rubber-benzene system have been extended over the whole concentration range, a plot of the relative vapour pressures does not provide the most stringent test in the region of very dilute solutions. We now present some alternative ways of comparing the experimental results with the theory.

The entropy of mixing

4.7. The experimental results in which the relative pressures are measured make it possible to determine the partial molar free energies of mixing directly. To calculate the entropy of dilution, or the partial molar entropy of mixing, it is necessary to determine the heat of mixing. If ΔH is the heat absorbed on mixing N_1 molecules of solvent with N_r molecules of polymer, then the heat of dilution or the partial molar heat of mixing is given by

$$\Delta H_1 = L\left(\frac{\partial \Delta H}{\partial N_1}\right)_N. \tag{4.16}$$

The entropy of dilution is therefore given by

$$T\Delta S_1 = \Delta H_1 - \Delta G_1, \tag{4.17}$$

where ΔG_1 is determined by equation (4.5). Now, in terms of the volume fraction v_r of the r-mer molecules, equation (4.5) can be rewritten as

$$\frac{\Delta G_1}{RT} = \log(1-v_r) - \tfrac{1}{2}z\log\left\{1-\frac{2}{z}\left(1-\frac{1}{r}\right)v_r\right\}. \tag{4.18}$$

Measurements of heats of mixing of very low molecular homologues of rubber with various solvents plotted against the volume fraction of one of the components give an almost parabolic curve,† which is the form expected on Hildebrand's theory. Thus

$$\Delta H = \alpha v_1 v_r, \tag{4.19}$$

where α is a constant whose value according to Hildebrand‡ is given by

$$\alpha = (\surd E_1 - \surd E_r)^2, \tag{4.20}$$

where E_1 and E_r are the cohesive energy densities of the two species. Equation (4.19) leads on differentiation to the result

$$\Delta H_1 = \alpha \bar{V}_1 v_r^2, \tag{4.21}$$

where $\bar{V}_1$ is the partial molar volume of the liquid in the solution, so that

$$\frac{\Delta S_1}{v_r^2} + \frac{\Delta G_1}{T v_r^2} = \frac{\alpha \bar{V}_1}{T}. \tag{4.22}$$

In a similar fashion one can obtain a relation between the entropy, free energy, and heat of concentration; thus

$$\frac{\Delta S_r}{v_1^2} + \frac{\Delta G_r}{T v_1^2} = \frac{\alpha \bar{V}_r}{T}. \tag{4.23}$$

4.8. For a system with zero energy of mixing the free energy of mixing and the entropy of mixing are related by the equation

$$\Delta G = -T\Delta S,$$

so that for the partial molar entropy of mixing the theory gives

$$\frac{\Delta S_1}{R} = \log(1-v_r) - \tfrac{1}{2}z\log\left\{1-\frac{2}{z}\left(1-\frac{1}{r}\right)v_r\right\}, \tag{4.24}$$

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† Ferry, J., Gee, G., and Treloar, L. R. G., *Trans. Faraday Soc.* 41 (1945), 341.

‡ Hildebrand, J. H., and Wood, S. E., *J. Chem. Phys.* 1 (1933), 817; Hildebrand, J. H., *Solubility of Non-Electrolytes*, Chemical Catalogue Co., New York, 1936.

corresponding to equation (4.18) for the free energy. A test of the theory can therefore be provided by plotting the sum of $\Delta S_1/v_r^2$, determined from equation (4.24), and $\Delta G_1/Tv_r^2$, determined from the vapour-pressure measurements, against the volume fraction v_r of the solute. According to equation (4.22) this quantity should be constant. It should be noted, however, that such a test depends not only on the validity of the theory of solutions of high polymers which has been developed so far, but also on that of Hildebrand's theory of the heat of mixing of liquids. The free energies of dilution of natural rubber by a number of liquids have been calculated† from vapour-pressure and from osmotic-pressure measurements,‡ and the entropies of dilution have been calculated from equation (4.24) for $z = 5$. The results are plotted in Fig. 6, from which it is clear that, for mixtures of

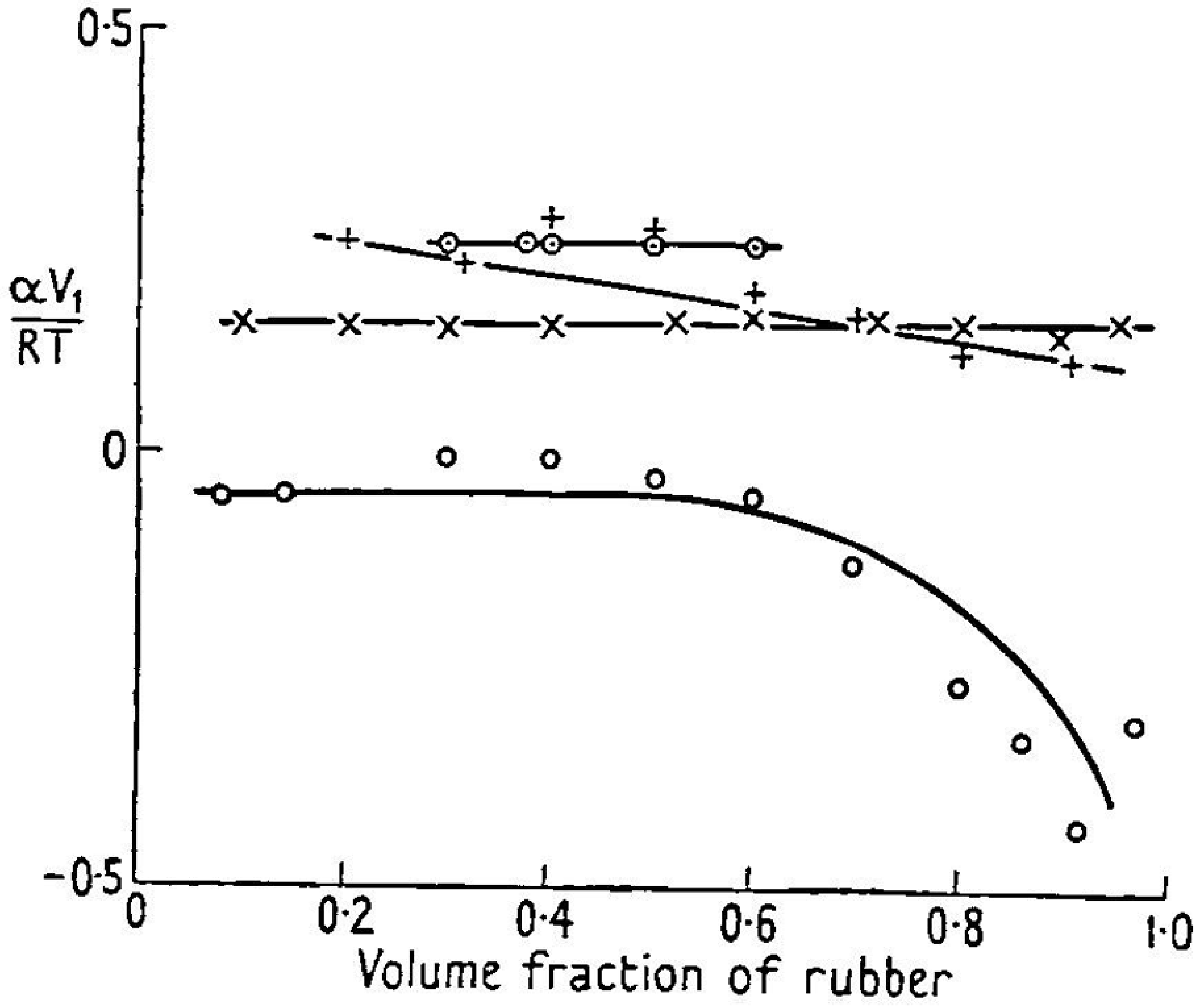

FIG. 6. $\alpha V_1/RT$ for different solvents as a function of the volume fraction of rubber; × benzene, + toluene, ⊙ carbon disulphide, ○ chloroform.

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† Gee, G., *Advances in Colloid Science*, **2** (1946), 165.

‡ The sources of the vapour-pressure data are: benzene (Gee, G., and Treloar, L. R. G., *Trans. Faraday Soc.* **38** (1942), 147); carbon tetrachloride, chloroform Lens, J., *Rec. Trav. Chim.* **51** (1932), 971); toluene (Boissonnas, C. G., and van ler Wyk, A. J., *Helv. Chim. Acta*, **20** (1937), 779); carbon disulphide (Stamberger, P., *J. Chem. Soc.* (1929), 2318); and of the osmotic-pressure data are: arbon tetrachloride, chloroform, toluene (Posnjak, G., *Koll.-Beihefte*, **3** 1912), 417).

natural rubber in a number of solvents, $\alpha V_1/RT$ is nearly constant for a wide range of values of v_r. An alternative method of testing the constancy of

$$\frac{\Delta S_1}{v_r^2}+\frac{\Delta G_1}{Tv_r^2}$$

has been used extensively by Huggins.† He has shown that a wide range of data on polymer-liquid systems can be represented by an equation of the form

$$-\frac{\Delta G_1}{RT}=\frac{(\Delta S_1)_\infty}{R}-\nu v_r^2, \tag{4.25}$$

where $(\Delta S_1)_\infty$ is the limit to which ΔS_1, given by equation (4.24), tends as z approaches ∞, that is,

$$(\Delta S_1)_\infty=-R\left[\log(1-v_r)+\left(1-\frac{1}{r}\right)v_r\right], \tag{4.26}$$

and ν is assumed to be a constant. Equations (4.25) and (4.26) imply that if a function Φ is defined by

$$\Phi=\frac{1}{v_r}\left[\frac{\Delta G_1}{RT}-\log(1-v_r)\right]-\left(1-\frac{1}{r}\right),$$

then

$$\Phi=\nu v_r,$$

and, furthermore, from equation (4.22),

$$\nu=\frac{\alpha V_1}{RT} \tag{4.27}$$

in that region of concentration for which $(\Delta S_1)_\infty$ is a sufficiently good approximation to ΔS_1. It is evident by comparing equations (4.24) and (4.26) that ν will neither satisfy equation (4.27) nor will it be independent of v_r. In fact, equation (4.25) provides only a rather insensitive test of the thermodynamical data on polymer-liquid systems. This insensitiveness of the method of plotting specified by equation (4.25) can be demonstrated by plotting Φ as a function of the volume fraction of polymer. From such curves it is evident‡ that neither the value of z nor of $\alpha V_1/T$ could be deduced even approximately in this way. A more direct way of testing equation (4.22) is by using measured values of the free energy of dilution with measured values of the heat of dilution to determine the entropy of dilution in accordance with equation (4.17) and to compare the results with the values calculated from equation (4.24). This we now do.

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† Huggins, M. L., *Ann. New York Acad. Sci.* 43 (1942), 1; *Ind. Eng. Chem.* 35 (1943), 216.

‡ Compare Gee, G., *Advances in Colloid Science*, 2 (1946), 145, Fig. 11.

4.9. Measurements have been made† of the heats of dilution of natural rubber with a number of liquids. For most of them $\Delta H_1/v_r^2$ was sensibly constant throughout the whole range of volume concentrations over which measurements were made. These measurements were combined with the free energy of dilution of natural rubber by the same liquids, calculated from the available vapour-pressure data. The results for the hydrocarbons, in the liquids which were investigated (benzene, heptane, and toluene), are plotted in Fig. 7. The curves are calculated from equation (4.24) for $z = 4$ and $z = 6$. It is evident that the estimated entropies of dilution are generally of the form predicted by the theory but are not in complete quantitative agreement with it. At least, however, these results indicate a semi-quantitive agreement between the theory of polymer solutions and the thermodynamical quantities determined experimentally.

It should also be noted that some part of the disagreement may arise from errors in the heats of dilution determined experimentally. In fact, the heat of dilution of rubber by benzene, which was used in calculating the experimental points in Fig. 7, did not agree with an earlier determination by the same workers.‡ Further measurements were therefore made§ of the heat of dilution of natural rubber by benzene.‖ There is a considerable scatter of the experimental points, so that the measurements are not accurate enough to determine the precise shape of the curve. Nevertheless, they suggest that the heat of dilution of natural rubber by benzene increases continuously with the volume fraction of the rubber, that is, decreases with increasing

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† Ferry, J., Gee, G., and Treloar, L. R. G., *Trans. Faraday Soc.* **41** (1945), 340.

‡ Gee, G., ibid. **38** (1942), 418.

§ Gee, G., and Orr, W. J. C., ibid. **42** (1946), 507.

‖ Of the solvents for which experimental points are plotted in Fig. 7, benzene is the only one for which a re-determination of the heat of dilution has been carried out.

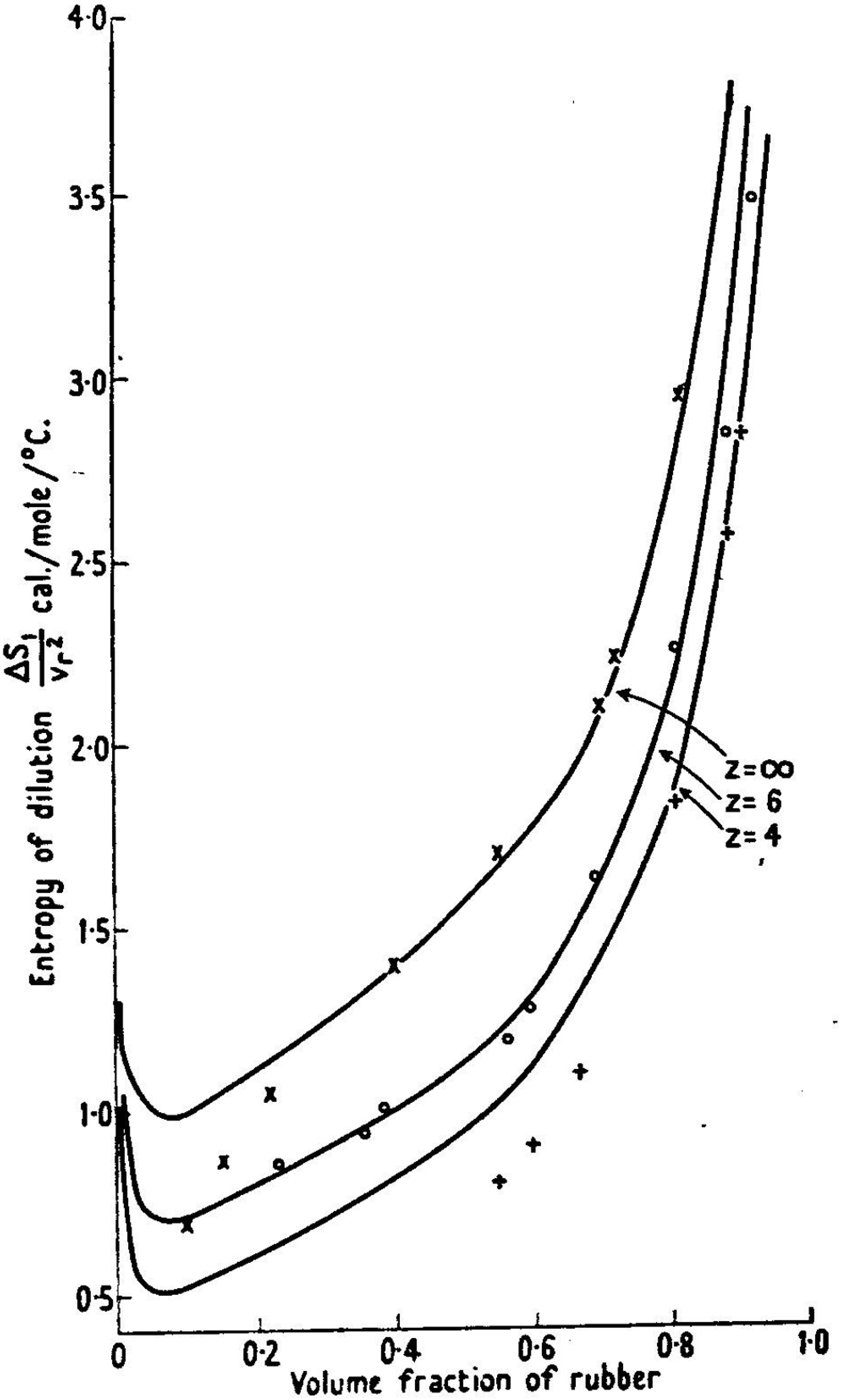

Fig. 7. Entropy of dilution of natural rubber with different solvents. The full curves are calculated from the theory with the values of z indicated. The experimental points refer to benzene (×) at 25° C., heptane (○) at 40° C., toluene (+) at 25° C.

dilution. From a reasonable curve drawn through the experimental points† Gee and Orr recalculated the experimental value of the partial molar entropy. This is represented by the full curve in Fig. 8, while the dotted curve is calculated from equation (4.24) with $z = 6$. It can be seen that although for volume fractions of rubber greater than about 0·25 the two curves have the same general shape, there is not complete agreement between them. At low rubber concentrations there is an appreciable discrepancy between the shapes of the experimental and the theoretical curves. In particular, the point of inflexion in the experimental curve in the neighbourhood of $v_r = 0{\cdot}25$ has no counterpart in the theoretical curve. This is the main point of disagreement between the theory and the experimental results; apart from this both curves are of the same general shape. The agreement between the measurements of vapour

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† See Fig. 9 below.

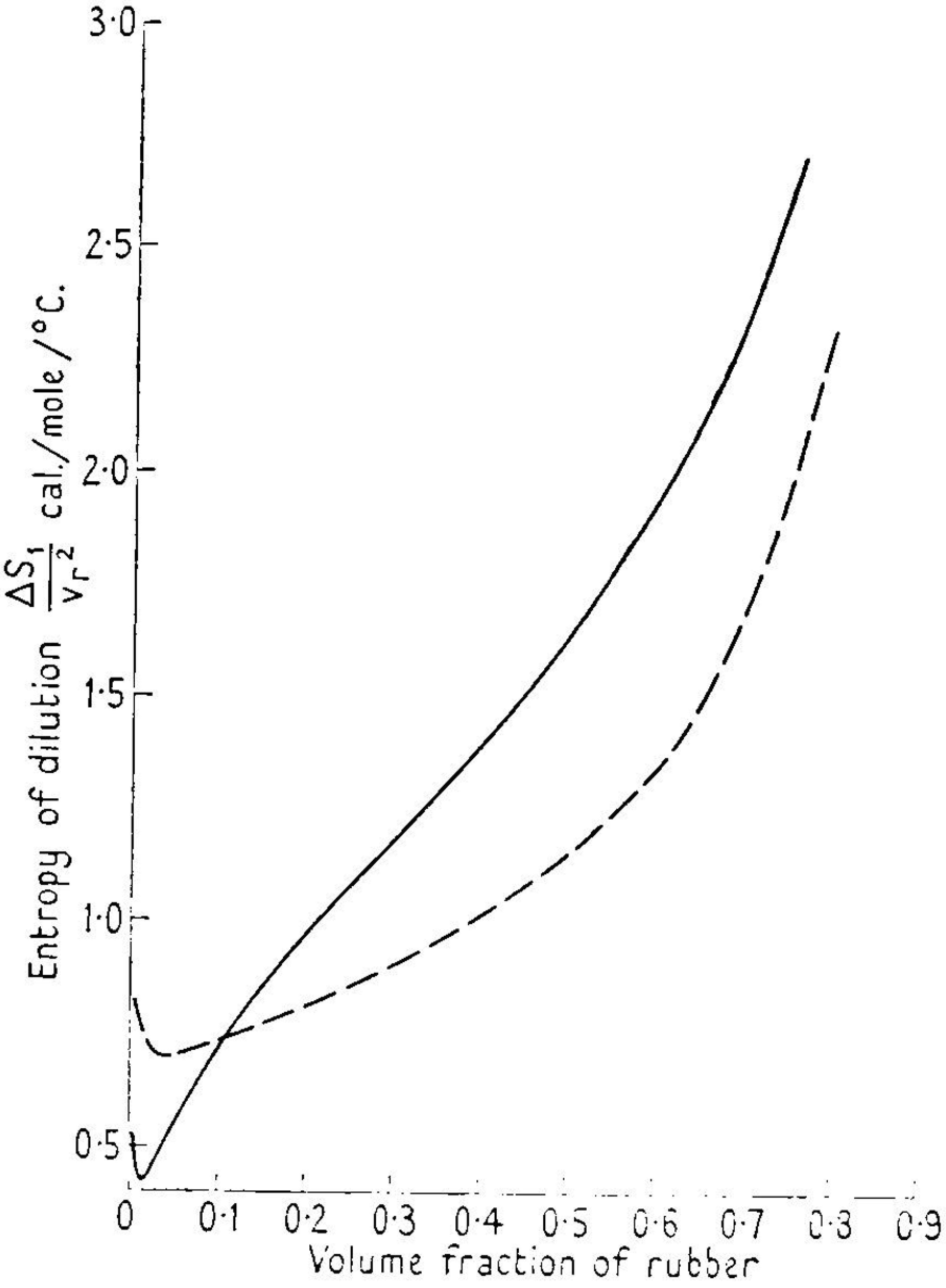

FIG. 8. Variation of the partial molar entropy of dilution of natural rubber with benzene with the volume fraction of rubber; ——— smoothed experimental results, - - - - theoretical curve.

pressure and the vapour-pressure curve calculated from equation 4.9) is evidence that the free energy of dilution accords reasonably well with that calculated from the theory. The discrepancy between the entropy of dilution calculated from the measured vapour pressure and that given by the theory must therefore be due to the measured fall in the value of $\Delta H_1/v_r^2$ as v_r decreases as shown in Fig. 9. If a direct plot of $\Delta G_1/Tv_r^2$ against v_r is made from the measured vapour pressures there is no point of inflexion in the neighbourhood of $v_r = 0{\cdot}25$ (compare Figs. 4 and 5 above). In view of this and of the evident uncertainty in the measurements of the heat of mixing, it is apparent that the discrepancy between the experimental and the theoretical curves for the entropy of dilution, as shown in Fig. 8, should not be accorded too great weight.

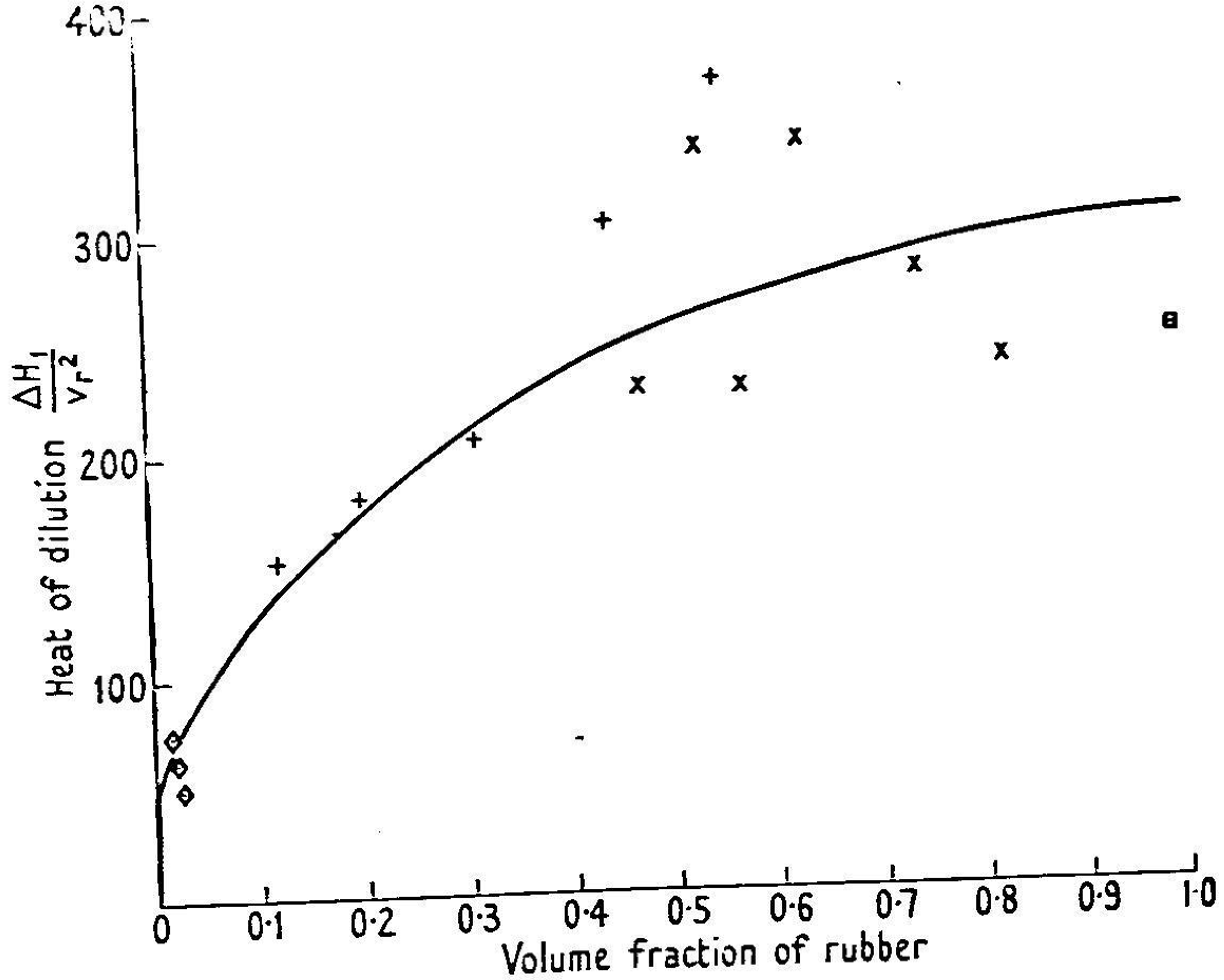

FIG. 9. Experimental values of the heat of dilution of natural rubber with benzene; × vapour-pressure data, + isopiestic data, ◇ osmotic data, ⊡ low vapour-pressure data.

4.10. In this connexion there is a further point to be noted.

therefore gives a value for the free energy directly. In the experiments, measurements are made of the vapour pressure of the solution compared with that of the pure solvent. This measurement determines the free energy of mixing directly. With measurements of the heat of mixing, the entropy of dilution as plotted in Fig. 8 can be derived from it. It must, however, be noted, as is clear from the preceding remarks, that the experimental and theoretical values of the entropy of dilution plotted in Fig. 8 are not strictly comparable. Both in the experimental work and the theory the primary quantity is the free energy of mixing. Consequently, irrespective of the reliance which can be placed on the measured values of the heat of mixing, greater weight should be given to the agreement between the free energy determined by experiment and calculated from the theory (Figs. 3, 4, and 5) than to the divergences between the derived values of the entropy (Fig. 8). It is concluded that in view of the elementary nature of the physical model which is employed in the theory, and of the assumption of random mixing (which assumes zero energy of mixing), the agreement between the theory and experiment is remarkably good. Certainly, the semi-quantitative agreement which has been found indicates that the main cause of the wide departures from Raoult's law shown by solutions of high polymers is to be sought in the effects of differences in molecular sizes and shapes.

4.11. It is clear, however, that it is desirable to determine the effect of a non-zero energy of mixing. For if the point of inflexion which is given by the experimental results, and arising from the experimental values of the heat of mixing, is a real effect, then it should also be manifest when the effect of a non-zero heat of mixing is examined theoretically. To do this it is necessary to evaluate the more general combinatory factor $g(N_i, X_{ij})$. This is the subject-matter of the next chapter.

V

THEORY OF MIXTURES WITH NON-ZERO ENERGY OF MIXING

5.1. In an earlier chapter of this work the combinatory factor $g(N_i)$ which occurs in the partition function of a mixture with zero energy of mixing and which contains simple chain, branched chain, or closed ring molecules has been evaluated. In order that the effect of a non-zero energy of mixing on the vapour-pressure equations and the other thermodynamical quantities can be determined it is necessary to evaluate the combinatory factor, denoted by $g(N_i, X_{ij})$, which occurs in the partition function for mixtures with non-zero energy of mixing (equation (1.34)). It is clear that Bethe's method could be used, for it was precisely to take account of interactions between neighbouring particles that it was devised. In determining $g(N_i)$ a set of partial differential equations, one equation to every component of the mixture, corresponding to equation (3.38), is obtained, and this set of equations is sufficient to determine $g(N_i)$ as a function of the N_i. When there is a non-zero energy of mixing there are, in addition, a set of partial differential equations, as many equations as there are quantities X_{ij}, corresponding to equation (3.39). The complete set of partial differential equations (3.38) and (3.39) are sufficient to determine $g(N_i, X_{ij})$ as a function of the N_i and the X_{ij}, provided that the conditions of integrability of the form

$$\frac{\partial}{\partial N_i}\log \eta_{ij} = \frac{\partial}{\partial X_{ij}}\log \epsilon_i \quad (\text{all } i), \tag{5.1}$$

$$\frac{\partial}{\partial N_j}\log \epsilon_i = \frac{\partial}{\partial N_i}\log \epsilon_j \quad (\text{all } i, j), \tag{5.2}$$

are satisfied. In these equations ϵ_i, ϵ_j are the parameters introduced in Bethe's method corresponding to the occupation of a site by a molecule of the type specified by the suffix and η_{ij} has been written for $\exp(-w_{ij}/z\boldsymbol{k}T)$, where w_{ij} is the energy of mixing. This method was first used† to determine the combinatory factor for mixtures of two species of monomer molecules and of monomer molecules with dimer molecules. However, the results can be derived in a more straightforward manner using the methods of chemical kinetics; in this connexion this method has been called the condition of quasi-chemical equilibrium.† This equation was first put forward in the consideration of non-ideal solutions of a class, defined as regular solutions (§ 1.12). The method is, in fact, equivalent to Bethe's approximation, and we now proceed to give an account of it and to demonstrate their equivalence.

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† Chang, T. S., *Proc. Cambridge Phil. Soc.* **35** (1939), 265.

Condition of quasi-chemical equilibrium

5.2. The configurational factor in the partition function for a strictly regular solution has been derived in § 1.13. With suitable choice of the energy zero it is given, for a binary mixture, by

$$\Omega(T) = \frac{1}{N_i!\,N_j!}\int\ldots\int e^{-w_{ij}X_{ij}/kT}(d\omega_i)^{N_i}(d\omega_j)^{N_j}. \qquad (5.3)$$

It was also pointed out in § 1.15 that if a quantity $\bar{\bar{X}}_{ij}$ is defined by

$$e^{-w_{ij}\bar{\bar{X}}_{ij}/kT}\int\ldots\int(d\omega_i)^{N_i}(d\omega_j)^{N_j} = \int\ldots\int e^{-w_{ij}X_{ij}/kT}(d\omega_i)^{N_i}(d\omega_j)^{N_j}, \qquad (1.30)$$

then the evaluation of the integral in equation (5.3) is reduced to the determination of $\bar{\bar{X}}_{ij}$.

Early workers in the theory of solutions commonly assumed that if $z\bar{\bar{X}}_{ij}$ is the average number of closest neighbour i—j pairs, then a sufficiently good estimate of $\bar{\bar{X}}_{ij}$ is equal to $\bar{X}$ given by

$$\bar{X}^2 = (N_i-\bar{X})(N_j-\bar{X}), \qquad (5.4)$$

where now, since we are dealing with binary mixtures, the suffixes to X can be omitted. From equation (5.4), $\bar{X}$ is necessarily independent of T. Since $z\bar{X}$ is the average number of i—j pairs, the numbers of i—i and j—j pairs respectively are $\frac{1}{2}z(N_i-\bar{X})$ and $\frac{1}{2}z(N_j-\bar{X})$, the factor one-half being introduced to take account of the fact that each i—i pair involves two molecules of type i. The physical meaning of equation (5.4) is therefore that the numbers of i—i, i—j, and j—j pairs are determined simply by the numbers of molecules of different types. It thus corresponds to the assumption of completely random mixing and can be strictly valid only for systems with zero energy of mixing. It is therefore a somewhat crude approximation for other cases. Since the integral on the left-hand side of equation (1.30) is the configurational term for a random mixture of the two species, denoted by $g(N_i)$, the configurational free energy of the system must be

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† Guggenheim, E. A., *Proc. Roy. Soc.* A **148** (1935), 304.

$$kT\log g(N_i)+\bar{\bar{X}}w. \tag{5.5}$$

If the combinatory factor for a mixture with non-zero energy of mixing be denoted, in our usual notation, by $g(N_i, \bar{X})$, then the configurational free energy of mixing is

$$kT\log g(N_i, \bar{X})+\bar{X}w. \tag{5.6}$$

Since, in general, $g(N_i, \bar{X})$ is necessarily different from $g(N_i)$, it follows that $\bar{X}$ and $\bar{\bar{X}}$ are necessarily different. It has been seen that to assume that $\bar{X}$ is given by equation (5.4) implies that there is completely random mixing so that the combinatory factor must reduce to $g(N_i)$. Thus if $z\bar{X}$ given by equation (5.4) is assumed to be the average value of the number of i—j pairs, then

$$\bar{X} = \bar{\bar{X}}. \tag{5.7}$$

From equation (1.32) it follows that when $\bar{X}$ is independent of T then $\bar{\bar{X}}/T$ can differ from $\bar{X}/T$ by, at most, an additive constant independent of T. The physical argument given above indicates that in this case the constant of integration which is introduced when equation (1.32) is integrated must be zero. It will be seen below (§ 5.6) that when $g(N_i, X)$ is evaluated and the value of $\bar{X}$ given by equation (4) is substituted for X, then $g(N_i, X)$ does in fact reduce to $g(N_i)$, which confirms equation (5.7).

5.3. It has been seen that equation (5.4) corresponds to the assumption of completely random mixing. An alternative formula which has been proposed† is

$$(N_i-\bar{X})(N_j-\bar{X}) = \bar{X}^2e^{-2w/zkT}, \tag{5.8}$$

where $\bar{X}$ is now a function of T and there is no longer a simple

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† Guggenheim, E. A., *Proc. Roy. Soc.* A **148** (1935), 304.

relation between $\bar{X}$ and $\bar{\bar{X}}$, as is evident from equations (5.5) and (5.6). Equation (5.8) is clearly based on the equations of chemical kinetics, and, even if it is not exact, it should at least be an improvement on equation (5.4). If the symbol i—j is used to denote a pair of sites occupied by segments of two different molecules, one of type i and the other of type j, then the rearrangement of the molecules which occurs when an i—i pair and a j—j pair are destroyed and two new i—j pairs are created can be represented symbolically by

$$(i—i)+(j—j) \rightarrow 2(i—j). \tag{5.9}$$

Equation (5.9) recalls the formula for a chemical reaction; if it did represent a chemical reaction between molecules, the equilibrium condition would be

$$\frac{X_{ij}^2}{4X_{ii}X_{jj}} = e^{-2w_{ij}/zkT}. \tag{5.10}$$

Although the equilibrium with which one is concerned in the arrangement of molecules is not that of a chemical reaction, it is not unreasonable to expect that the equilibrium condition between i—i, i—j, and j—j pairs should take a similar form. It was on this basis that equation (5.8) was proposed in investigating the properties of regular solutions. When a relation such as equation (5.8) or equation (5.10) is applied to the numbers of neighbouring sites which are occupied in various ways, it can be conveniently referred to as a condition of 'quasi-chemical' equilibrium. It should be emphasized† perhaps that although equations (5.8) and (5.10) have the same form as the law of mass action in chemical reactions, it is the relation of a given molecule to the surrounding structure, not its relation to another molecule, which is being considered.

In applying the method of chemical kinetics, by introducing the condition of quasi-chemical equilibrium, to derive the properties of regular solutions, Guggenheim did not distinguish between $\bar{X}$ and $\bar{\bar{X}}$. That their identification was invalid when $\bar{X}$ is given by equation (5.8) was pointed out by Rushbrooke‡ cf. § 5.2), who also showed that in this case the condition of quasi-chemical equilibrium could be derived from the approximate formula for the grand partition function obtained by Bethe's method. It was later shown that, for particles each of which occupies only one site of the array, the condition of quasi-chemical equilibrium and Bethe's equations are equivalent for all regular assemblies† and also for assemblies with long-range order.‡ More recently, their equivalence has been shown also for assemblies of particles each of which occupies more than one site on the array.§ The latter demonstration, which is the one mmediately relevant to the purpose of this monograph, will now be considered.

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† Cf. Bragg, W. L., and Williams, E. J., ibid. A **145** (1934), 669.

‡ Rushbrooke, G. S., ibid. A **166** (1938), 296.

Equivalence of Bethe's method and the condition of quasi-chemical equilibrium

5.4. The equivalence of Bethe's method and the condition of quasi-chemical equilibrium for mixtures which contain polymer molecules can be shown in the following way. Let (i, i, S) denote the term in the grand partition function, constructed according to Bethe's method, in which the central site of the group of sites which is considered in detail and a selected first shell neighbour are occupied by segments of different molecules of type i and all the remaining sites are occupied in some specified manner denoted by S; define (j, j, S) in a similar manner. Let (i, j, S) denote the term in which the central site and the selected first shell site are occupied by segments of molecules of types i and j respectively with all the other sites occupied in the manner S; likewise let (j, i, S) denote the converse manner of occupation of the central site and the selected first shell site. One of the essential approximations of Bethe's method is the assumption that the ratios $(i, i, S)/(i, j, S)$ and $(j, i, S)/(j, j, S)$ are independent of S. This follows from the way in which the parameters of Bethe's method are introduced and is clear from the considerations of § 3.7. In fact, the parameters ϵ and η which occur in Bethe's method can be defined by

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† Guggenheim, E. A., *Proc. Roy. Soc.* A **169** (1938), 134.

‡ Fowler, R. H., and Guggenheim, E. A., ibid. A **174** (1940), 189.

§ Guggenheim, E. A., ibid. A **183** (1944), 213.

$$\frac{(i,i,S)}{(i,j,S)} = \frac{\epsilon}{\eta}, \tag{5.11}$$

$$\frac{(j,i,S)}{(j,j,S)} = \epsilon\eta. \tag{5.12}$$

A further set of quantities can be defined in the following way. Denote the sum of all the terms in the grand partition function constructed according to Bethe's method, corresponding to the occupation of the central site and the selected first shell site by segments of different molecules of type i by (i,i); define (j,j) in a like manner. Denote by (i,j) the sum of all the terms in the grand partition function in which the central site is occupied by a segment of a molecule of type i, and the selected first shell site is occupied by a segment of a molecule of type j; likewise define (j,i) as the sum of all the terms corresponding to the converse manner of occupation of the central site and the selected first shell site. Since the left-hand members of equations (5.11) and (5.12) are independent of S, then summation over all configurations S yields the equations

$$\frac{(i,i)}{(i,j)} = \frac{\epsilon}{\eta}, \tag{5.13}$$

$$\frac{(j,i)}{(j,j)} = \epsilon\eta. \tag{5.14}$$

The central site and the selected first shell site are chosen arbitrarily; consequently they are necessarily physically equivalent. Their physical equivalence implies

$$(i,j) = (j,i), \tag{5.15}$$

and consequently

$$\frac{\{(i,j)+(j,i)\}^2}{4(i,i)(j,j)} = \eta^2. \tag{5.16}$$

The frequency with which a particular mode of occupation of the sites of the array occurs is proportional to the corresponding term in the grand partition function. Thus (i,i), which is the sum of a number of terms in the grand partition function, must be proportional to the frequency with which the selected pair of sites is occupied by segments of two different molecules of type i; likewise for (i,j), (j,i), and (j,j). The central site and the selected first shell site are chosen in an arbitrary manner and are physically indistinguishable from any other pair of sites in the array. Thus the frequency with which they are occupied in a given mode is proportional to the frequency with which closest neighbour pairs, of the kind specified by that mode of occupation, occur throughout the assembly. Thus

$$(i,i):(i,j)+(j,i):(j,j) = X_{ii}:X_{ij}:X_{jj}. \tag{5.17}$$

Equation (5.17) identifies equation (5.16) with the condition of quasi-chemical equilibrium provided only that

$$\eta = \epsilon^{-w_{ij}/zkT}, \tag{5.18}$$

which is precisely the value assigned to η in Bethe's approximation. This establishes the equivalence of the two methods.

Free energy of a polymer-solvent system

5.5. We now consider how the condition of quasi-chemical equilibrium, that is, the method of chemical kinetics, can be applied to binary mixtures in which one of the constituents is a high polymer.† The generalization of the condition of quasi-chemical equilibrium, equation (5.8), to a binary mixture of monomer and r-mer molecules is

$$(N_1-\bar{X})(qN_r-\bar{X}) = \bar{X}^2\epsilon^{2w/zkT}, \tag{5.19}$$

where, as previously defined, w is the energy of mixing and zq is the number of closest neighbour interactions in which each r-mer molecule takes part. The solution of equation (5.19) is

$$\bar{X} = \frac{2X^*}{1+\beta}, \tag{5.20}$$

where X^* is the limit to which $\bar{X}$ tends as w approaches zero. Thus X^* is the solution of the equation

$$(N_1-\bar{X})(qN_r-\bar{X}) = \bar{X}^2$$

which is appropriate to completely random mixtures. This gives

$$X^* = \frac{qN_1N_r}{N_1+qN_r}.$$

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† Orr, W. J. C., *Trans. Faraday Soc.* **40** (1944), 320.

Also, β, which is defined by

$$\beta = \left\{1+\frac{4X^*}{N_1+qN_r}(e^{2w/zkT}-1)\right\}^{\frac{1}{2}}, \tag{5.21}$$

is a function of T. From equation (1.32), $\overline{\overline{X}}$ is then given by

$$\overline{\overline{X}} = 2X^*T\int\limits_{\infty}^{1/T}\frac{d(1/T)}{1+\beta}. \tag{5.22}$$

Changing the variable of integration from $1/T$ to β yields

$$\overline{\overline{X}} = \frac{2X^*zkT}{w}\int\limits_{1}^{\beta}\frac{\beta\,d\beta}{(1+\beta)(\beta^2-\kappa^2)}, \tag{5.23}$$

where κ is defined by

$$\kappa^2 = \left(\frac{N_1-qN_r}{N_1+qN_r}\right)^2.$$

Integration of equation (5.23) gives the result†

$$\overline{\overline{X}} = \frac{X^*zkT}{w}\left\{\frac{1}{1+\kappa}\log\frac{2(\beta-\kappa)}{(1-\kappa)(1+\beta)}+\frac{1}{1-\kappa}\log\frac{2(\beta+\kappa)}{(1-\kappa)(1+\beta)}\right\}, \tag{5.24}$$

where the constant of integration has been determined from the fact that, when the energy of mixing is zero (that is, β is unity), $\overline{\overline{X}}$ and $\overline{X}$ are equal, and each reduces to X^*. That the value of $\overline{\overline{X}}$ given by equation (5.24) satisfies the required conditions can be verified by using equation (1.32) to obtain $\overline{X}$ from it with the help of the relation

$$\frac{d\beta}{d(1/T)} = \frac{w}{zk}\frac{\beta^2-\kappa^2}{\beta}$$

and thus recovering equation (5.20). This general result was given by Orr; an approximate solution for a mixture of two different kinds of monomers had been given earlier by Rushbrooke.‡ By expanding the radical in equation (5.21) and retaining the first three terms, an expression for $\bar{X}$ equivalent to Rushbrooke's approximation is obtained; thus

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† Ibid.

‡ Rushbrooke, G. S., *Proc. Roy. Soc.* A **166** (1938), 296.

$$\bar{X} = \frac{2X^*}{1+\beta} = \frac{(N_1+qN_r)(\beta-1)}{2(\epsilon^{2w/z\boldsymbol{k}T}-1)} = X^*\left\{1-\frac{X^*}{N_1+qN_r}(\epsilon^{2w/z\boldsymbol{k}T}-1)\right\}. \tag{5.25}$$

To the same order of approximation, we have

$$\bar{\bar{X}} = X^*\left[1-\frac{X^*}{N_1+qN_r}\left\{\frac{z\boldsymbol{k}T}{2w}(\epsilon^{2w/z\boldsymbol{k}T}-1)-1\right\}\right], \tag{5.25$'$}$$

in which the constant of integration has been determined by the fact that for zero energy of mixing $\bar{\bar{X}}$ reduces to X^*[†].

5.6. From equation (1.30) the contribution to the free energy of mixing due to the non-zero energy of mixing is given by

$$\Delta A_\epsilon = \Delta G_\epsilon = \bar{\bar{X}}w, \tag{5.26}$$

while the heat or energy of mixing is given by

$$\Delta H = \Delta E = \bar{X}w. \tag{5.27}$$

In addition to ΔA_ϵ or ΔG_ϵ arising from the non-zero energy of mixing, there are contributions to the free energy of mixing due to the combinatory factor in the partition function; these are given by equation (3.62). The total configurational free energy of mixing is therefore

$$\Delta A = \Delta G = \Delta A_\epsilon + \Delta A_c, \tag{5.28}$$

where $$\Delta A_c = \log g(N_1, N_r)/g(0, N_r).$$

From the remarks made in connexion with equations (5.5) and (5.6) above it will be clear that this use of the condition of quasi-chemical equilibrium is, in fact, equivalent to the evaluation of the combinatory factor $g(N_i, X_{ij})$ in terms of the combinatory factor $g(N_i)$ which has been determined previously. Presentation of the explicit formulae to which equations (5.27) and (5.28) with equations (5.20) and (5.21), or approximately with equations (5.25) and (5.25$'$), lead will be deferred until the combinatory factor $g(N_i, X_{ij})$ has been determined directly in terms of $g(N_i)$ with the help of the condition of quasi-chemical equilibrium.[†]

[†] Misprints in Orr's equations (10) and (14) should be noted, as also a mistake in sign in the expression for $\bar{X}$ immediately following Rushbrooke's equation (6).

5.7. The evaluation of $g(N_i, X_{ij})$ by direct methods is prohibitively difficult in the general case. However, it is possible to set down certain general considerations which $g(N_i, X_{ij})$ must satisfy, and, with the help of the conditions of quasi-chemical equilibrium, these are sufficient to determine the form of $g(N_i, X_{ij})$ unambiguously in terms of $g(N_i)$. We now state the conditions.

(i) To ensure that the free energy of a system of a given temperature and composition shall be proportional to the size of the system it is necessary that $\{\log g(N_i, X_{ij})\}/\sum_i N_i$ must be homogeneous and of zero degree in the N_i.

(ii) To ensure that the free energy of the assembly is a continuous function of its configurational energy W in the neighbourhood of $W = 0$ it is necessary that, when W is zero, $g(N_i, X_{ij})$ should reduce to $g(N_i)$, apart from terms negligible compared with N_i.

(iii) It will be assumed that the conditions for maximizing

$$g(N_i, X_{ij})\exp\{-W(X_{ij})/kT\}$$

with respect to X_{ij} are equivalent to the conditions of quasi-chemical equilibrium between the alternative methods of occupation of a pair of neighbouring sites. The argument can be presented generally for a mixture with any number of components of molecules of any type—simple, simple chain, branched chain, or closed ring. In presenting the general argument the notation which has been specified in Chapter II is used.

The condition of quasi-chemical equilibrium, equation (5.10), can be written in the form

$$\Big(q_i N_i - \sum_k{}' X_{ik}\Big)\Big(q_j N_j - \sum_k{}' X_{jk}\Big) = X_{ij}^2 e^{2w_{ij}/zkT} \qquad \text{(all } i,j \text{ with } i \neq j) \quad (5.29)$$

by using equation (2.3). Quantities X_{ij}^* are introduced with meanings corresponding to that assigned to X^* in § 5.5. That is, X_{ij}^* is the solution of the equation

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[†] Guggenheim, E. A., *Proc. Roy. Soc.* A **183** (1944), 213.

$$\Big(q_i N_i - \sum_k{}' X_{ik}\Big)\Big(q_j N_j - \sum_k{}' X_{jk}\Big) = X_{ij}^2$$

whence

$$X_{ij}^* = \frac{q_i q_j N_i N_j}{\sum_k q_k N_k} \quad \text{(all } i, j), \tag{5.30}$$

and likewise the quantities X_{ii}^* are given by

$$X_{ii}^* = \frac{(q_i N_i)^2}{\sum_k q_k N_k} \quad \text{(all } i). \tag{5.30$'$}$$

It is now possible to construct an expression for the number of distinguishable configurations of all the molecules in which the configurational energy has a given value, that is, the X_{ij} have given values. The formula for $g(N_i, X_{ij})$ determined by the three considerations set out above is

$$\log g(N_i, X_{ij}) = \log g(N_i) + \sum_i \log\frac{(zX_{ii}^*)!}{(zX_{ii})!} + \sum_{i,j}{}' \log\frac{(zX_{ij}^*)!\, 2^{zX_{ij}}}{(zX_{ij})!\, 2^{zX_{ij}^*}}, \tag{5.31}$$

where $g(N_i)$ is given by equation (3.68). It can be seen from equations (5.30) that the X_{ij} are homogeneous and of the first degree in the N_i, from which it follows that $\{\log g(N_i, X_{ij})\}/\sum_i N_i$ given by equation (5.31) is homogeneous and of zero degree in the N_i. From the definition of the X_{ij}^* it is evident that when all the w_{ij} are zero $g(N_i, X_{ij})$ reduces to $g(N_i)$. Finally, if

$$\log\{g(N_i, X_{ij})\exp(-W/kT)\} = \log g(N_i, X_{ij}) - \sum_{i,j}{}' w_{ij} X_{ij}/kT$$

is maximized with respect to X_{ij}, the condition which is obtained is

$$\tfrac{1}{2}z\log\Big(q_i N_i - \sum_k{}' X_{ik}\Big) + \tfrac{1}{2}z\log\Big(q_j N_j - \sum_k{}' X_{jk}\Big) - z\log X_{ij} -$$

$$- w_{ij}/kT = 0 \quad (i \neq j),$$

which is precisely the condition of quasi-chemical equilibrium, equation (5.29). Thus equation (5.31) for $g(N_i, X_{ij})$ satisfies the conditions required for the combinatory factor. It can be simplified by substituting in equation (5.31) the values of X_{ij}^* given by equation (5.30) and of $g(N_i)$. For simple or branched chain molecules equation (5.31) assumes the form

$$\log g(N_i, X_{ij}) = \sum_i N_i \log \rho_i - \sum_i \log N_i! + z \sum_i \log(q_i N_i)! -$$
$$-(\tfrac{1}{2}z-1)\log\Bigl(\sum_i r_i N_i\Bigr)! - \tfrac{1}{2}z \sum_i \log\Bigl(q_i N_i - \sum_k{}' X_{ik}\Bigr) -$$
$$-z \sum_{i,j}{}' \log X_{ij}. \quad (5.32)$$

5.8. The free energy of the assembly is given by

$$A = -kT \sum_i N_i \phi_i - kT \log g(N_i, \bar{X}_{ij}) + z \sum_{i,j}{}' w_{ij} \bar{X}_{ij}, \quad (5.33)$$

where ϕ_i is the partition function for a molecule of type i for all kinds of energy apart from the configurational energy, and $\bar{X}_{ij}$ denotes the equilibrium value of X_{ij} determined by equation (5.29). Equations (5.32) and (5.33) yield, for the free energy of the assembly (at negligible pressures),

$$\frac{G}{kT} = \frac{A}{kT} = \sum_i N_i \log \phi_i \rho_i + \sum_i \log N_i! - z \sum_i \log(q_i N_i)! +$$
$$+(\tfrac{1}{2}z-1)\log\Bigl(\sum_i r_i N_i\Bigr)! + \tfrac{1}{2}z \sum_i \log\Bigl(q_i N_i - \sum_k{}' \bar{X}_{ik}\Bigr) +$$
$$+z \sum_{i,j}{}' \log \bar{X}_{ij} + \sum_{i,j}{}' w_{ij} \bar{X}_{ij}. \quad (5.34)$$

From this all the thermodynamical properties can be derived. In particular the partial potentials μ_i and the absolute activities λ_i can be obtained by differentiating equation (5.34) with respect to N_i. Since $\partial A/\partial \bar{X}_{ij}$ is zero for all i, j, variations in $\bar{X}_{ij}$ may be ignored in carrying out this differentiation. Thus, one derives

$$\frac{\mu_i}{kT} = \log \lambda_i = -\log \phi_i \rho_i + \log N_i - zq_i \log q_i N_i +$$
$$+(\tfrac{1}{2}z-1)r_i \log \sum_k r_k N_k + \tfrac{1}{2}zq_i \log\Bigl(q_i N_i - \sum_{i,k}{}' \bar{X}_{ik}\Bigr), \quad (5.35)$$

which leads to

$$\lambda_i = \frac{N_i}{\phi_i \rho_i} \frac{\Bigl(\sum_k r_k N_k\Bigr)^{(\frac{1}{2}z-1)r_i} (2\bar{X}_{ii})^{\frac{1}{2}zq_i}}{(q_i N_i)^{zq_i}} \quad (5.36)$$

for simple chain and branched chain molecules.

These equations for the partial potentials lead immediately to the vapour-pressure equations. Specifying the partial vapour pressure of the component i in the mixture by p_i and the vapour pressure of the pure liquid by $p_{i,0}$, then

$$\frac{p_i}{p_{i,0}} = \frac{r_i N_i}{\sum\limits_k r_k N_k}\left\{\frac{2q_i \bar{X}_{ii} \sum\limits_k r_k N_k}{r_i(q_i N_i)^2}\right\}^{\frac{1}{2}zq_i}$$

$$= \frac{r_i N_i}{\sum\limits_k r_k N_k}\left\{\frac{q_i\Big(q_i N_i - \sum\limits_{i,k}{}' \bar{X}_{ik}\Big)\sum\limits_k r_k N_k}{r_i(q_i N_i)^2}\right\}^{\frac{1}{2}zq_i}. \tag{5.37}$$

In these formulae the values of the q_i are given in equation (2.1) and the $\bar{X}_{ik}$ are given by the solutions of the equations of quasi-chemical equilibrium which are determined by the set of equations (5.29). These cannot generally be solved explicitly. Further simplification is possible only for a binary mixture.

5.9. When there are only two types of molecules, specified by i and j in the mixture, equation (5.32) reduces to

$$g(N_i, N_j, X)$$

$$= \frac{\rho_i^{N_i}\rho_j^{N_j}\{(q_i N_i)!\}^z\{(q_j N_j)!\}^z}{N_i!\,N_j!\{(r_i N_i + r_j N_j)!\}^{\frac{1}{2}z-1}\{(q_i N_i - X)!\}^{\frac{1}{2}z}(X!)^z\{(q_j N_j - X)!\}^{\frac{1}{2}z}} \tag{5.38}$$

and equation (5.34) reduces to

$$\frac{G}{kT} = \frac{A}{kT} = N_i \log\phi_i\rho_i - N_j \log\phi_j\rho_j + \log N_i! + \log N_j! -$$

$$-z\log(q_i N_i)! - z\log(q_j N_j)! + (\tfrac{1}{2}z-1)\log(r_i N_i + r_j N_j)! +$$

$$+z\log X! + \tfrac{1}{2}z\log(q_i N_i - X)! + \tfrac{1}{2}z\log(q_j N_j - X)! + wX, \tag{5.39}$$

where the suffixes have been dropped from w_{ij}, X_{ij} as there can be no risk of confusion by so doing. Formulae equivalent to equations (5.38) and (5.39) had already been obtained in three special cases when Guggenheim deduced the general formulae for mixtures containing simple or branched chain molecules.

Chang† had used Bethe's approximation in a way similar to that described in § 3.7 to examine the two simple cases

$$r_i = r_j = q_i = q_j = \rho_i = \rho_j = 1$$

and

$$r_i = 2, \quad q_i = 2(z-1)/z, \quad \rho_i = z/2, \quad r_j = q_j = \rho_j = 1.$$

Orr‡ had used the condition of quasi-chemical equilibrium as described in §§ 5.5 and 5.6 to obtain the free energy of mixing for a system containing monomer and simple chain molecules, that is, for the case

$$r_i = r, \quad q_i = (rz-2r+2)/z, \quad r_j = q_j = \rho_j = 1.$$

5.10. For this latter case the absolute activities are given by equation (5.36) with the appropriate values of the r_i and q_i. Using the notation of § 5.5 for such a binary mixture we obtain

$$\lambda_1 = \frac{N_1}{\phi_1(N_1+rN_r)}\left\{\frac{(N_1+rN_r)(N_1-\bar{X})}{N_1^2}\right\}^{\frac{1}{2}z}, \tag{5.40}$$

$$\lambda_r = \frac{N_r}{\phi_r\,\rho_r(N_1+rN_r)}\left\{\frac{(N_1+rN_r)(qN_r-\bar{X})}{(q_r N_r)^2}\right\}^{\frac{1}{2}zq}, \tag{5.41}$$

where $\bar{X}$ is the solution of equation (5.19). Using the parameters κ and β, which have been introduced in § 5.5, these expressions reduce to

$$\lambda_1 = \frac{N_1}{\phi_1(N_1+rN_r)}\left\{\frac{2(N_1+rN_r)(\beta-\kappa)}{(N_1+qN_r)(1+\beta)(1-\kappa)}\right\}^{\frac{1}{2}z}, \tag{5.42}$$

$$\lambda_r = \frac{N_r}{\phi_r\,\rho_r(N_1+rN_r)}\left\{\frac{2(N_1+rN_r)(\beta+\kappa)}{(N_1+qN_r)(1+\beta)(1+\kappa)}\right\}^{\frac{1}{2}zq}. \tag{5.43}$$

If $\lambda_{1,0}$, $\lambda_{r,0}$ denote the values of the absolute activities for the pure substance we obtain

$$\frac{\lambda_1}{\lambda_{1,0}} = \frac{N_1}{N_1+rN_r}\left\{\frac{2(N_1+rN_r)(\beta-\kappa)}{(N_1+qN_r)(1+\beta)(1-\kappa)}\right\}^{\frac{1}{2}z}, \tag{5.44}$$

$$\frac{\lambda_r}{\lambda_{r,0}} = \frac{N_r}{N_1/r+N_r}\left\{\frac{2(N_{1/r}+N_1)(\beta+\kappa)}{(N_1/q+N_r)(1+\beta)(1+\kappa)}\right\}^{\frac{1}{2}zq}. \tag{5.45}$$

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† Chang, T. S., *Proc. Cambridge Phil. Soc.* **35** (1939), 265.

‡ Orr, W. J. C., *Trans. Faraday Soc.* **40** (1944), 320.

The relation between the partial potentials and the absolute activities is

$$\frac{\lambda_i}{\lambda_{i,0}} = \exp(\mu_i - \mu_{i,0})/kT,$$

and, for equilibrium with the vapour phase, the right-hand side of this equation is the ratio of the partial pressure of species i above the mixture to the vapour pressure of the pure species i. Thus equations (5.44) and (5.45) give the vapour-pressure equations.

Furthermore, at negligible pressures, the free energy of the mixture is given by

$$\frac{A}{kT} = \frac{G}{kT} = N_1 \log \lambda_1 + N_r \log \lambda_r.$$

With equations (5.42) and (5.43) this gives

$$A = A_c + A_e,$$

where

$$\begin{aligned}\frac{A_c}{kT} &= -\log g(N_1, N_r) - N_1 \log \phi_1 - N_r \log \phi_r \\ &= -N_1 \log \phi_1 - N_r \log \phi_r \rho_r + \log N_1! + \log N_r! - \\ &\quad -\tfrac{1}{2}z \log(N_1 + qN_r)! + (\tfrac{1}{2}z - 1)\log(N_1 + rN_r)! \end{aligned} \tag{5.46}$$

and

$$\begin{aligned}\frac{A_e}{kT} = \tfrac{1}{2}z(N_1 + qN_r)\Big\{(1-\kappa)\log\frac{\beta-\kappa}{(1+\beta)(1-\kappa)} &+ \\ +(1+\kappa)\log\frac{\beta+\kappa}{(1+\beta)(1+\kappa)}\Big\}&. \end{aligned} \tag{5.47}$$

When the energy of mixing is zero, β is unity and A_e vanishes. It may therefore be regarded as the part of the free energy due to the energy of mixing. For the free energies of mixing we obtain contributions

$$\begin{aligned}\frac{\Delta A_c}{kT} &= (\tfrac{1}{2}z - 1)(N_1 + rN_r)\log(N_1 + rN_r) - \\ &\quad -\tfrac{1}{2}z(N_1 - qN_r)\log(N_1 + qN_r) + \tfrac{1}{2}zN_r \log q/r, \end{aligned} \tag{5.48}$$

and

$$\frac{\Delta A_e}{kT} = z(N_1+qN_r)\left\{(1-\kappa)\log\frac{2(\beta-\kappa)}{(1+\beta)(1-\kappa)}+\right.$$
$$\left.+(1+\kappa)\log\frac{2(\beta+\kappa)}{(1+\beta)(1+\kappa)}\right\}. \quad (5.49)$$

These are the values already deduced by Orr in his treatment of this particular case; that equation (5.49) is identical with equation (5.26) can be seen by substituting the value of X^* in equation (5.24).

The value of $\bar{X}$ on the assumption of the condition of quasi-chemical equilibrium is given in equation (5.20). Thus the heat of mixing is given by

$$\Delta E = \Delta H = \bar{X}w = \frac{1-\kappa^2}{2(1+\beta)}(N_1+qN_r)w. \quad (5.50)$$

The entropy of mixing is given by

$$T\Delta S = \Delta E - \Delta A, \quad (5.51)$$

where ΔE is given by equation (5.50) and ΔA is the sum of ΔA_c given by equation (5.48) and of ΔA_e given by equation (5.49).

Effect of non-zero energy of mixing on agreement with experiment

5.11. The values of the entropy of mixing calculated in this way can be used to examine whether taking into account the non-zero energy of mixing improves the agreement between the experimental and theoretical determinations.† From the expression for ΔG the partial potentials can be determined for various values of z and of w. Typical results are shown in Fig. 10. From this diagram it follows that values of w greater than about 500 calories correspond to highly insoluble systems; furthermore, large negative values of w are unlikely for hydrocarbon systems. The best agreement with the experimental results, for reasonable values of z, is shown with w about 200 calories. The curves in Fig. 10 imply that in comparing the experimental and theoretical determinations of the entropy of mixing a value of w not greater than about 500 calories should be assumed. In fact, such a value will show the maximum difference which a non-zero energy of mixing can introduce.

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† Orr, W. J. C., *Trans. Faraday Soc.* **40** (1944), 320.

Making such calculations from equations (5.48), (5.49), and (5.50) $T\Delta S_1$ can be determined as a function of the volume fraction v_r of the rubber. For volume fractions of rubber less than

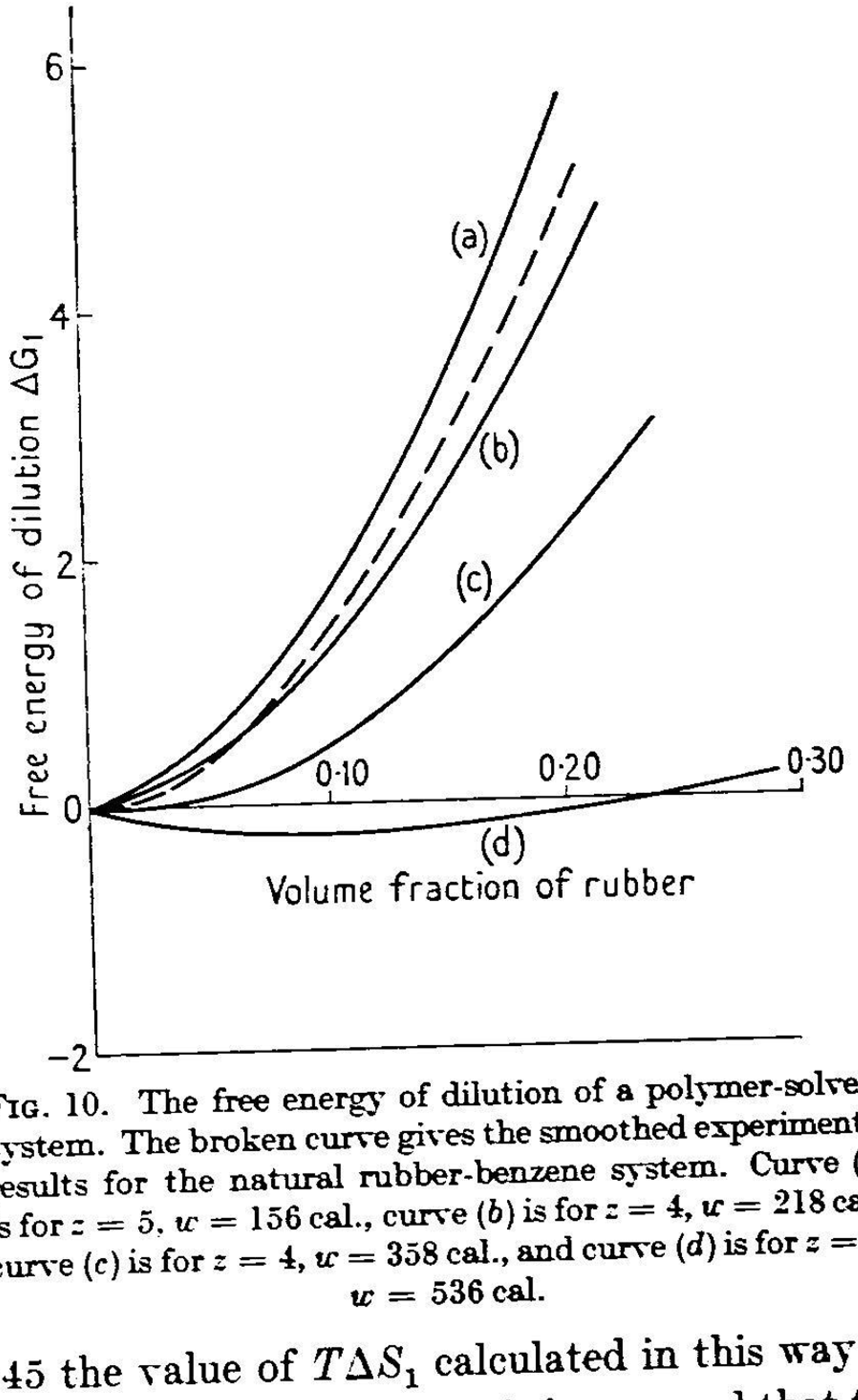

Fig. 10. The free energy of dilution of a polymer-solvent system. The broken curve gives the smoothed experimental results for the natural rubber-benzene system. Curve (*a*) is for $z = 5$, $w = 156$ cal., curve (*b*) is for $z = 4$, $w = 218$ cal., curve (*c*) is for $z = 4$, $w = 358$ cal., and curve (*d*) is for $z = 4$, $w = 536$ cal.

about 0·45 the value of $T\Delta S_1$ calculated in this way is greate than that which is obtained when it is assumed that the energ of mixing is zero. On the other hand, for v_r greater than 0·45 th value of $T\Delta S_1$ is less than that calculated from the elementa theory in which the energy of mixing is disregarded. When is recalled that the latter gave values of ΔS_1 higher than tho determined by experiment for dilute solutions and that it ga olutions rich in rubber, it will be seen that, over the greater part f the concentration range, the values of ΔS_1 calculated from quations (5.48), (5.49), and (5.50) are not in quite so good agree-nent with the experimental values as those derived from the lementary theory which neglects the energy of mixing. The

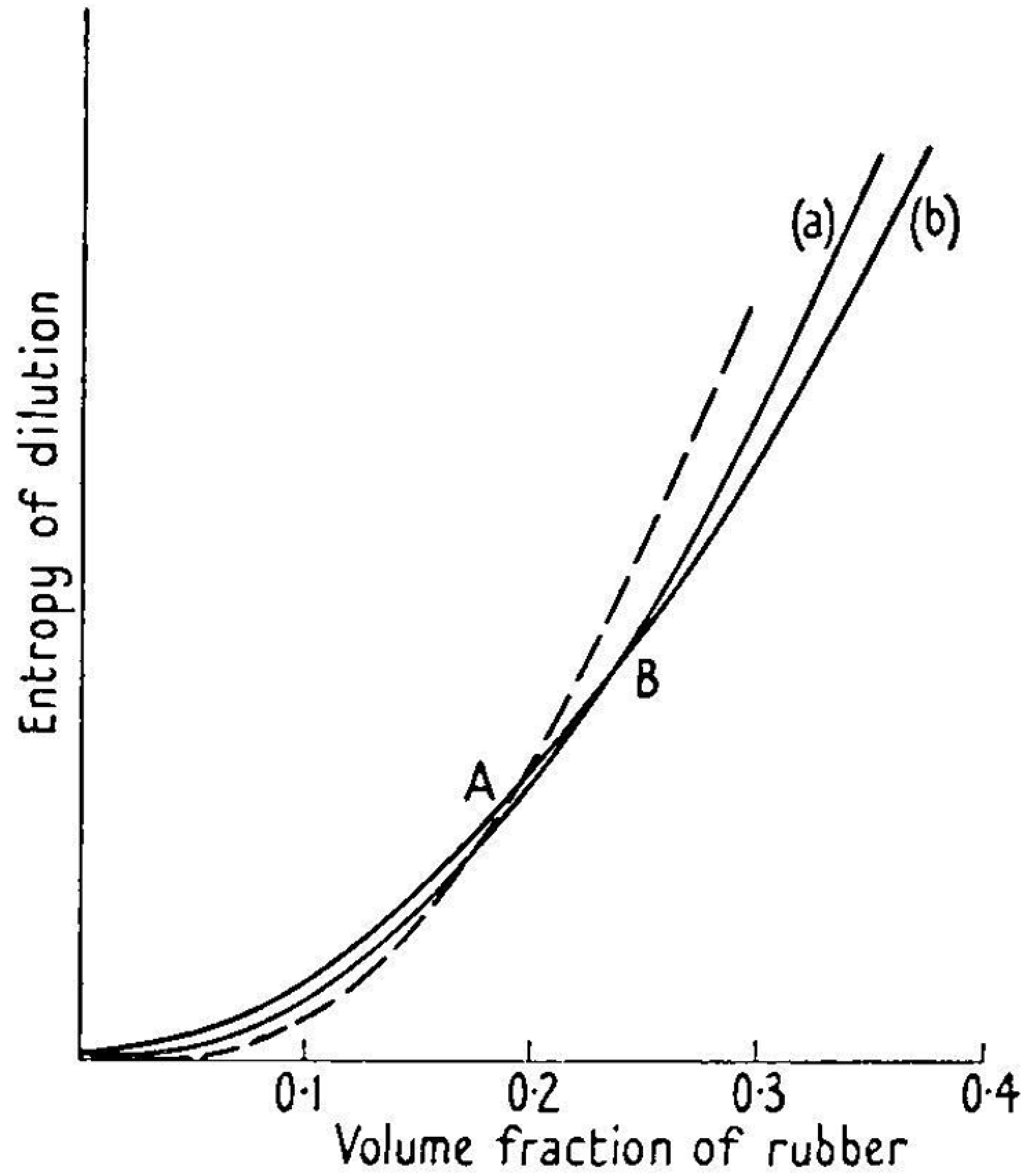

FIG. 11. Schematic diagram to show the effect of the energy of mixing on the entropy of dilution. Curve (a) is for a random mixture of molecules, curve (b) is for a mixture with a non-zero energy of mixing, and the broken curve shows the experimental values.

ate of affairs is shown schematically in Fig. 11, in which curves) and (b) and the dotted curve respectively represent the results otained by the theories disregarding and taking account of the on-zero energy of mixing and the experimental results. It is ear that only between the points of intersection A and B of ese curves can the curve calculated from the theory which cludes the effect of a non-zero energy of mixing give better greement with the experimental results. In particular, in the gion of dilute solution where the discrepancy between the ementary theory and the experimental results is greatest, lowance for the energy change on mixing does nothing to

5.12. It should also be noticed that the theoretical curve hich is obtained when the non-zero energy of mixing is taken to account is of the same shape as that for a mixture with zero nergy of mixing. In particular, the theory which takes account f a non-zero energy of mixing gives no indication of any point

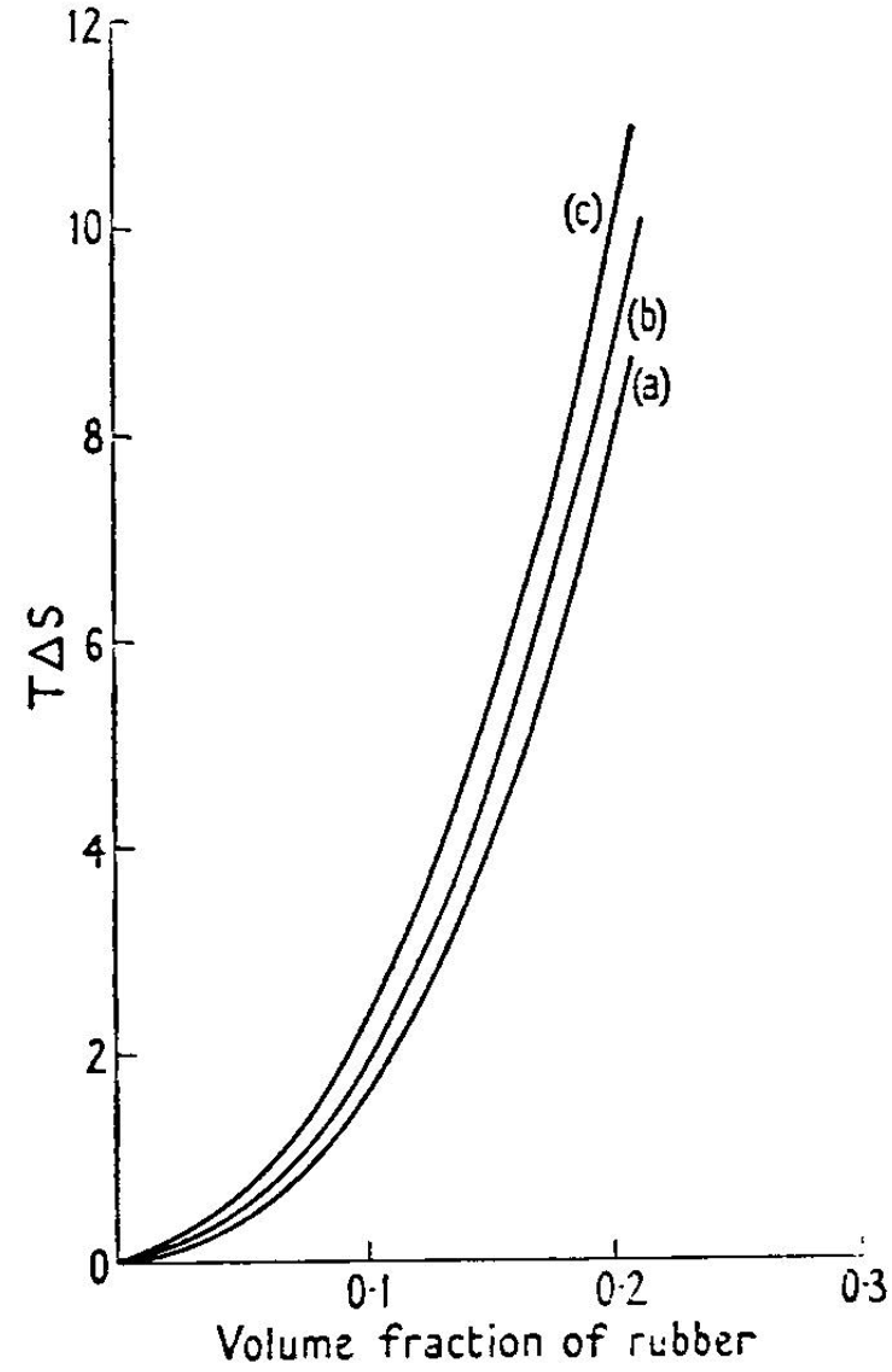

FIG. 12. The entropy of dilution of rubber-benzene mixtures in the region of dilute solution. Curve (*a*) shows the experimental results, curve (*b*) is the theoretical curve for a random mixture, and curve (*c*) is for the energy of mixing (w) equal to 536 cal.; the theoretical curves are calculated for $z = 6$.

f inflexion in the curves which are obtained by plotting $\Delta S_1/v_r^2$ s a function of the volume fraction of the polymer (v_r) in the eighbourhood of $v_r = 0{\cdot}25$. It has already been seen that the point of inflexion at this point in the experimental curves arises from the variation in the heat or energy of dilution deduced from xperiment (Fig. 9). That, theoretically, a non-zero heat of mixing does not have such an effect would appear to cast doubt on the validity of the variation of the heat of dilution as used by Gee (and shown in Fig. 9) and suggests that the shape of the curve for the entropy of dilution, deduced from these measurements, must be viewed with some reserve. In view of the wide scatter of the experimental points for the heat of mixing it is unlikely that a firm conclusion could be reached without more precise measurements of this quantity. In the meantime, however, it provides another reason, additional to those given in §§ 4.9 and 4.10, why greater weight should be given to the agreement between the measured and calculated free energies for polymer-solvent systems than to the apparent divergence, for volume fractions of polymer less than about 0·25, between the measured and calculated values of the entropy.

The introduction of a non-zero energy of mixing gives no better agreement with the experimental data than is given by the simple theory of a random mixture which takes account simply of the differences in size and shape of the molecules of the constituent species. Thus the heat or energy of mixing *in itself* cannot provide an explanation of the shape of the entropy curve for dilute solutions. It should, however, be noted that the analysis which has been given to include the effect of a non-zero heat or energy of mixing assumes that the configurational properties of the polymer molecules are essentially the same for all volume fractions of polymer. This point will be discussed in §§ 6.3–6.5 below.

5.13. Another important conclusion can be drawn from these calculations. Even with the maximum value of the energy of mixing which is compatible with the existence of a solution, the maximum deviation of ΔS_1, calculated from equations (5.48), (5.49), and (5.50), from the value which is predicted by the theory which assumes completely random mixing is not more than about 25 per cent. It follows that for a system in which the polymer is just soluble in the solvent the differences in the calculated values of the entropy are not likely to be more than about 20 per cent.; thus, the assumption of random mixing does not introduce a very serious error, particularly in comparison with other possible errors which are inherent in the nature of the physical model which is used in the theory of liquids. This analysis provides a justification of the original assumption that in a first approximation it was reasonable to consider a system with zero energy of mixing. It also indicates that the greater part of the divergence between the experimental results and the elementary theory which assumes random mixing must be due to some factor other than the non-zero energy or heat of mixing. To a consideration of some of these factors and of the errors which are implicit in the physical model of a liquid we must now turn in the closing chapter of this monograph.

VI

CRITICISMS AND EXTENSIONS OF THE THEORY

6.1. IT has been seen that the introduction of a non-ze energy of mixing in the elementary theory of polymer-liqu mixtures developed in Chapter III is unable to account for t differences between this theory and the experimental result We shall now consider some other possible causes of the di crepancy between the theory of solutions of high polymers a the experimental results. This examination will also serve indicate those aspects of the behaviour of solutions of polyme on which further research is required. Implicit in the applicati of the theory to a particular system such as the rubber-benze mixture is an assumption that the benzene molecule and t isoprene unit are sufficiently nearly the same size and shape th each can be allocated to one site of the quasi-crystalline arr without serious error. Another source of error may be due to t tendency, at least in very dilute solution, towards cluster form tion due to self-coiling of the rubber molecules.

In this chapter we will first examine the effects of these t factors. Following this an indication of the effect of the appro mate methods which have been used to construct the partiti function will be considered. Finally, certain implications of t physical model on which the theory is based will be considere

The effect of allocating one site each to a benzene molecule and to an isoprene unit

6.2. It has been noted that implicit in the application formulae such as equation (3.47) to the rubber-benzene syste is the assumption that the benzene molecule and the isopre unit are approximately the same size and shape, so that ea can be allocated to one site without introducing any serio error. Bernal[†] has shown that for two sorts of spherical mo cules to pack together it is necessary that their molecular volum do not differ by a factor of more than two to one. Althou

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[†] Quoted by Fowler and Guggenheim, *Statistical Thermodynamics*, Ca bridge, 1939, § 814 f.n.

Bernal's calculation is for spherical molecules, it probably indicates approximately the volume ratio of molecules which depart not too greatly from a sphere and yet still pack together. In particular if the molecules of one kind are oblate spheroids whose shorter axis is the same as the diameter of the molecules of the other kind which are spherical, they will probably pack together if the other axes of the oblate spheroid do not differ from the shorter axis by a factor of more than about 1·4 to 1. In the course of another investigation Orr† examined the available data, from X-ray analysis and a knowledge of the extent of the van der Waals field, on the sizes and shapes of the benzene molecule and the isoprene unit. His conclusions were that the benzene molecule in the liquid phase was roughly an oblate spheroid in shape having major axes of about 6·0 to 6·3 A and a minor axis of about 4·0 to 4·3 A with an average coordination of between 6 and 8, and that the structure of rubber in the unextended state is probably fairly adequately represented by a roughly tetrahedral coordination of linked sub-groups with the distance between the centres of mass of neighbouring sub-groups about 4·4 A. The ratio of the major axis of the benzene molecule to this spacing lies between 1·36 and 1·43. These figures suggest that the allocation in our physical model of one site each to an isoprene unit and a benzene molecule may possibly lead to errors which would cause a divergence between the experimental and the theoretical results.

To get some idea of the effect which this difference has on the thermodynamical parameters of the system, the following model was examined.‡ The system was supposed to consist of N_r polymer molecules as before and of N_d disk-shaped molecules which are such that when one of them occupies a site, it precludes the occupation, by any other molecule, of those first shell sites which lie in one of the planes (through the occupied site) of maximum abundance of closest neighbour sites. For instance, for simple lattices this means that each disk-shaped molecule occupies a site and four of its closest neighbours, while the other $z-4$

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† Orr, W. J. C., *Trans. Faraday Soc.* **43** (1947), 12.

‡ Miller, A. R., unpublished results.

closest neighbour sites can be occupied by other molecules. For various small values of r Bethe's method was used to derive the partial differential equations which express the equilibrium of the system; these were then integrated to determine the corresponding combinatory factor; from these values a general expression could be written down (essentially a mathematical extrapolation) for any value of r.

The formulae obtained conform to the general formula (§ 3.25) for mixtures of any number of polymer molecules of different sizes (equation (3.68) above), with each disk-shaped molecule regarded as a molecule of five segments corresponding to the number of sites which it has been assumed to occupy. At first sight this might appear to be somewhat surprising, but further consideration shows that the model of a disk-shaped molecule which has been used is really indistinguishable from a four-branched molecule which occupies a site and four of its closest neighbours with one branch going to each of these closest neighbours. This is only a special case of a branched chain molecule for which equation (3.68) is known to be valid, and consequently on the physical model adopted for the disk-shaped molecules the general formula can be used with the appropriate values of the parameters.

When the entropy of mixing is calculated for this case it is found to differ little from that calculated on the assumption that a polymer segment and a solvent molecule each occupy one site. In particular, it is no more successful than the elementary theory in reproducing the shape of the experimental curve in the region of dilute solutions. This can be made evident without difficulty. For the free energy of mixing of the polymer and the disk-shaped molecules the equation

$$\frac{\Delta G_d}{R} = \log(1-v_r) - \tfrac{1}{2}zq_d \log\left\{1 - \frac{2}{zq_d}\left(1 - \frac{d}{r}\right)v_r\right\} \tag{6.1}$$

is obtained, while the corresponding formula for a monomer-polymer system can be derived by rewriting equation (4.5) in terms of v_r, giving

$$\frac{\Delta G_1}{R} = \log(1-v_r) - \tfrac{1}{2}z \log\left\{1 - \frac{2}{z}\left(1 - \frac{1}{r}\right)v_r\right\}. \tag{6.2}$$

For the cases of interest r is very large, in particular $r \gg d$. Inspection of equations (6.1) and (6.2) shows that in this case and for dilute solutions ΔG_d calculated from equation (6.1) differs only insignificantly from ΔG_1 calculated from equation (6.2). It must be concluded that the difference in size and shape between the disk-shaped molecules and the segments of the polymer affects the calculated thermodynamical functions hardly at all; *a fortiori*, the actual differences between a benzene molecule and an isoprene unit will be still less responsible for the differences between the elementary theory and experiment which have been noted in Chapter IV.

Self-coiling of polymer molecules

6.3. In polymer-liquid mixtures of moderate and high concentration in polymer the individual polymer molecules intertwine with one another so extensively that, even on a molecular scale, the availability of polymer segments is effectively uniform. On the other hand, at very high dilutions the polymer chains separate out from each other and tend to form clusters by coiling up. Two lines of evidence point to such cluster formation. By studying dielectric relaxation in mixtures[†] it has been shown that whereas normal mixtures show only a single loss maximum, mixtures which are near the point of separation into two phases show two maxima which must be due to considerable heterogeneity on a molecular scale. It has also been shown[‡] that for rubber-liquid mixtures $\Delta H_1/v_r^2$ falls rapidly with v_r, that is, as more liquid is imbibed. This can only mean that few liquid-rubber contacts are made by molecules of liquid which enter the mixture near the saturation limit.

The analysis of mixtures containing dimer and trimer molecules using Bethe's method allows for the flexibility of these molecules. The formal mathematical extrapolation involved in the deduction of a formula appropriate to mixtures containing polymer molecules could be expected to yield correct results provided that no new effects are introduced when molecules of high polymers are considered. Furthermore, it was also indicated

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[†] Schallamach, A., *Trans. Faraday Soc.* **42** A (1946), 180.

[‡] Gee, G. and Orr, W. J. C., ibid. **42** (1946), 507.

that provided the steric properties of the polymer molecules are the same in solution as in the pure species the additional configurations due to the flexibility of the polymer molecules contribute nothing to the configurational free energy of mixing. With very long chain molecules, however, and in very dilute solutions, the flexibility of the polymer molecules may well lead to effects which are inhibited in more concentrated solutions. Such an effect is the self-coiling of the polymer molecules, and it is not taken into account in the deduction of equation (3.47). Likewise in the derivation of the generalized combinatory factor for a completely random mixture by either statistical or kinetic methods, effects due to the self-coiling of the polymer molecules are disregarded in the assumption of complete randomness in the neighbourhood of a site occupied in a specified way. With very long polymer chains a segment of a polymer molecule may, as a result of the bending back of the molecule on itself, be competing for a site with a segment of the same molecule which has already been placed on the array of sites. The interpretation of complete randomness which has been adopted takes no account of such blocked configurations. This effect can, of course, arise only for long chains in which self-coiling occurs. It therefore appears that in very dilute solutions of high polymers aggregation into clusters occurs as a result of the self-coiling of the polymer molecules. The statistical treatments which have been given make no allowance for such effects. It therefore appears that the divergence between the theoretical and the experimental results in very dilute solutions is probably due to the coiling of the polymer molecules with the consequent introduction of self-interfering or blocking configurations.

6.4. On the basis of such a clustering of polymer molecules due to their coiling two attempts have been made to give a theory of very dilute polymer solutions. In one of these,† the region of space which is defined by a coiled polymer molecule is defined as the volume pervaded by a polymer molecule. A 'swelling' factor, in terms of which the thermodynamical quantities are

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† Flory, P. J., *J. Chem. Phys.* **13** (1945), 453.

measured, is defined as the ratio of the volume pervaded by the polymer molecule to its actual molecular volume; for flexible long chain molecules in solution this factor is very large. It is further assumed that, in very dilute solutions, those sites within the volume pervaded by the polymer molecule which are not occupied by segments of it are vacant. At moderate concentrations there is complete intertwining of the polymer molecules and every site is occupied either by a polymer segment or by a solvent molecule. It would appear that on such a model there must, at least for some concentrations, be a volume change on mixing which is contrary to the measurements which have been made† on the rubber-benzene system over the entire range of concentration. Consequently, this treatment is open to serious objection, and it appears that a more detailed analysis is necessary.

6.5. Orr‡ also considered the coiling of polymer molecules. As a first step in the analysis of the problem he examined the limit of infinite dilution. In this limit the problem is that of determining the average configuration of a set of effectively non-overlapping flexible polymer chains in thermal equilibrium in a solvent phase. Ultimately the problem is to determine the statistical average configuration of a single polymer molecule in a given force field environment. Orr derived a formula for the heat of mixing which contains terms corresponding to the heat of solution of a hypothetical non-interacting chain and to the energy change in the transition from this hypothetical state to the equilibrium coiled-up configuration. Taking account of closest neighbour interactions and steric self-blocking effects, he computed the average configuration of polymer molecules; this calculation was carried out accurately by direct counting for short chains but can only be done approximately, and in numerical terms, for long chains. Even so, this appears to be a more promising approach to the problem, for the following reason.

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† Posnjak, G., *Koll.-Beihefte* **3** (1912), 417; Gee, G., and Treloar, L. R. G., *Trans. Faraday Soc.* **38** (1942), 158.

‡ Orr, W. J. C., ibid. **43** (1947), 12.

Formally, the configurational term for a very dilute solution, in which the polymer molecules separate out individually and coil up, can be split up into a term to allow for the arrangement of the individual coiled polymer molecules and another term to give the number of configurations of each polymer on its cluster of sites on the quasi-crystalline array. It is the consideration of this latter problem that is the essence of this attempt to consider the limit of infinite dilution. Further progress appears to depend on its elucidation.

6.6. It has been noted in § 5.11 that taking account of a non-zero energy of mixing is unable to account for the point of inflexion which is obtained in the experimental curves in which $\Delta S_1/v_r^2$ is plotted as a function of the volume fraction of polymer. The theoretical curves which are obtained in this case are, in fact, of the same shape as those obtained for a random mixture. Thus ostensibly there is no reason on theoretical grounds why the heat or energy of mixing should vary in such a way that it introduces a point of inflexion into the curve of $\Delta S_1/v_r^2$ plotted as a function of v_r in the neighbourhood of $v_r = 0{\cdot}25$. It will be recalled, however, that the mathematical analysis given in Chapter V for a mixture with non-zero energy of mixing assumes that the configurational properties of the polymer molecules are independent of their concentration in the solution. In particular, no account is taken of the fact that it is likely that in dilute solutions the polymer molecules cluster to form aggregates. The comparison of the experimental and the theoretical results therefore suggests that the self-coiling of the polymer molecules in dilute solution, leading to their aggregation, affects the variation of the heat of dilution with the volume fraction of the polymer. This would account for the agreement between the free energy curves and the divergence, for dilute solutions, between the entropy curves. Thus it may be concluded that it is through the effect of the self-coiling of the polymer molecules on the variation of the heat of dilution that the divergence between the theoretical and experimental entropy curves arises for dilute solutions. Further research is therefore required to examine the effects of the self-coiling of the polymer molecules and, in particular, to examine how this affects the variation of the heat of dilution.

The quasi-crystalline model

6.7. It must be emphasized that the physical model of a liquid which has been used, and which is called a quasi-crystalline model, is one in which a high degree of local order, without necessarily any long-range order, is envisaged. Furthermore, the statistical methods which have been used in Chapters III and V consider the detailed occupation either of a pair or of a small group of neighbouring sites. In no case does the argument depend upon the existence of long-range order. On the basis of the absence of long-range order in a liquid there appears to be little justification for any suggestion that the statistical methods which have been used, although valid for solid solutions, are of more doubtful applicability to liquid mixtures.

These statistical methods do, however, assume that there is a constant coordination number which describes the local order of the quasi-crystalline array. How good an approximation to the partition function of the liquid mixture is provided by these statistical methods will depend on the extent of the fluctuations about the average coordination number. It is an essential assumption of the physical model of a liquid which has been adopted here, and which is currently accepted, that the fluctuations about the average coordination number, except perhaps in a negligible fraction of centres in the liquid, are far from able to disturb the regularity of the geometrical relationship between each molecule and its closest neighbours, that is, the short-range order. That this assumption is justified in a wide range of liquids has been verified by X-ray analysis.†

6.8. Apart from this, the assumption of a constant average coordination number may introduce difficulties in the application of the theory to particular systems, due to the fact that the pure liquids may have different coordination numbers. For rubber and benzene it has been shown† that the coordination numbers are probably a little greater than 4 and between 6 and 8 respectively. The assumption of a constant coordination number for the mixture may therefore be unduly restrictive in particular applications. However, in view of the small dependence on the coordination number of the calculated thermodynamical functions, as shown by the curves in Fig. 7, this would appear not to exercise any great influence.

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† Friedrich, W., *Phys. Zeit.* **14** (1913), 397; Debye, P., and Scherrer, P., *Gött. Nach* **16** (1916); Debye, P., and Menke, H., *Phys. Zeit.* **31** (1930), 797; *Ergeb. d. Tech. Röntgenk.* II (1931); Bragg, W. L., *The Crystalline State, A General Survey* (G. Bell and Sons, 1933), p. 195; Gingrich, N. S., *Rev. Mod. Phys.* **15** (1943), 90; Finbak, C., *Avh. norske Vidensk. Akad.* **10** (1945).

Statistical methods

6.9. It will be recalled that it has been shown that Bethe's method agrees with the power series expansion in terms of moments of the configurational energy as far as the limit to which these have been calculated (§ 3.1). Thus while the Bragg-Williams approximation corresponds to the first moment of the configurational energy, the equations which are obtained using either Bethe's method or the condition of quasi-chemical equilibrium correspond to an expansion as far as the third moment.

6.10. These methods are, though, approximate. It has been shown‡ that the computation of the partition function for one- and two-dimensional arrays can be reduced to an eigenvalue problem. The method, which involves most elegant mathematics, appears to be particularly suitable for examining those co-operative phenomena which exhibit transition points, such as order-disorder phenomena in alloys. It has the advantage that it can be computed exactly, but so far it has not proved possible to extend such analyses to a three-dimensional model. Furthermore, it assumes complete long-range order as in a crystal and consequently the method appears to be inapplicable to liquid mixtures. This latter restriction can, however, be removed,[†] although in the application of the method by which this is done to a three-dimensional model the results can only be computed numerically.

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† Orr, W. J. C., *Trans. Faraday Soc.* **43** (1947), 12, Appendix III; see § 6.2 above.

‡ Kramers, H. A., and Wannier, G. H., *Phys. Rev.* **60** (1941), 252, 263; Onsager, L., ibid. **65** (1944), 117; Wannier, G. H., *Rev. Mod. Phys.* **17** (1945), 50; Onsager, L., *Report on Conference of Physical Society at Cambridge*, 1946, **2** (1947), 137.

In this connexion two conclusions emerge from the considerations which have been examined in other sections of this monograph. The first is that mathematical refinement of the statistical calculation of the partition function is not the immediate need.[‡] The second is that closer agreement with experiment is to be sought rather in constructing a physical model which provides a better representation of a liquid.

Conclusion

6.11. The behaviour of solutions of high polymers is markedly different from that of solutions of low molecular substances. Solutions of high polymers show large divergences from the laws of ideal solutions. The theory which has been developed is based on a quasi-crystalline model of a liquid, in which there is a high degree of local order in the geometrical relations of a molecule and its near neighbours, but a complete absence of that long-range order which is characteristic of a crystal. The local order is defined by an average coordination number, and fluctuations about it are neglected. This picture accords with the available X-ray evidence on the structure of liquids. The existence of such local order and no long-range order is all that is required for the application of the statistical methods which have been used in developing the theory. Such a physical model cannot, though, claim to be precise and should probably be regarded as an approximation which is adequate for many purposes.

The statistical theory of random mixtures which has been developed in this monograph agrees, at least semi-quantitatively, with the experimental data. It accounts for the greater part of the differences between the behaviour of solutions of high polymers and of ideal solutions. It establishes that the greater part of this difference in behaviour is due to the difference in size and shape of the molecules of the constituent species.

[†] Domb, C., unpublished results.

[‡] Cf. Kirkwood, J. G., *J. Chem. Phys.* 8 (1940), 623.

The agreement between the experimental and theoretical free-energy curves is very good. However, when the entropy is calculated, using measured values of the heat of dilution, it is found that the variation of the latter quantity is such that a point of inflexion is introduced, for high dilution, into the experimental curves in which $\Delta S_1/v_r^2$ is plotted as a function of the volume fraction of the polymer. This is the point of least satisfactory agreement between the experimental results and the theory. In particular, introduction of a non-zero energy (or heat) of mixing into the theory fails to reproduce this effect. It has also been shown that this divergence is not due to the assumption that a solute molecule and a polymer segment are interchangeable and each occupies one site of the quasi-crystalline array, nor to the assumption of an average coordination number for the mixture. It should be pointed out, in this connexion, that the scatter of the experimental values of the heat of dilution is rather large, so that more precise measurements of this quantity would be desirable, before firm conclusions can be reached on this point. In the meantime greater weight should therefore be attached to the agreement between the experimental and theoretical free energy curves than to the divergence, in dilute solution, of the entropy curves. It is pointed out that there is evidence that in very dilute solutions the polymer molecules tend to coil up to form clusters. No such effect is taken into account in developing the theory which assumes that the configurational properties of the polymer molecules are independent of their concentration in the mixture. Thus it appears reasonable to conclude that the disagreement between the experimental results and the theory in the region of dilute solution is probably due to clustering of the polymer molecules; and, in particular, to the effect which such aggregation of the polymer molecules has on the variation of the heat of dilution. Examination of this point is a subject for further research.

That such good agreement exists between theory and experiment as has been shown in the preceding pages is evidence of the ‘striking advances in the mathematical treatment of the behaviour of long-chain molecules'[†] which have been made during the last decade. Further advances and more precise agreement are probably to be sought in a physical model which represents an actual liquid more faithfully than does the quasi-crystalline model, rather than in refinements of the mathematical and statistical techniques.

[†] *Nature*, **159** (1947), 734.

SUBJECT INDEX

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